# POROUS TRANSPARENT AEROGELS:
## Development of Superinsulating Window Technology
## Renewable Energy Branch

Prepared for:

Renewable Energy Branch
Energy, Mines and Resources Canada
Ottawa, Canada
DSS Contract File No: 23216-6-6257/01SZ
July, 1988

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**ACKNOWLEDGEMENTS**

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Funding for this project was provided by the Panel of Energy Research and Developoment, Office of Energy Research and Development, Energy, Mines and Resources Canada.

92-03840/

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## PREFACE

The Department of Energy, Mines and Resources has elected to sponsor research and development that will advance solar energy technology in Canada. The scope of the program ranges from basic materials investigation to commercial product testing. Broad topic areas include active solar technology, passive solar hybrid technology, photovoltaic technology, wind energy, and small scale/low head hydro. The development of insulating super window technology is within the domain of the second area, and is highly significant in that it possesses the potential to revolutionize the building industry worldwide. Aerogel is a light, transparent material that has excellent insulating characteristics. If produced cost-effectively, it would provide an ideal insulating filler for high R-value windows.

This document summarizes the work performed under contract number 23216-6-6257/0152 of the Solar Energy Development Program. The objective was to develop the freeze drying method of aerogel production to the point of demonstrating commercial viability. The report provides details of the experimental program, observed results, and a discussion of process improvements and limitations. Its intended purpose is to inform The Department of Energy, Mines and Resources of the status of the process development upon conclusion of the contract. Due to the proprietory nature of the work, the Contractors request that the report be placed under restricted circulation status.

**ABSTRACT**

The objective of this project was to develop and demonstrate the fundamental basis of a commercially viable process for the production of porous transparent aerogel superwindows. The work was based on the results of the project team's previous basic research in this field, and concentrated on the freeze drying process of cross-linked gels.

To this end, a rigorous experimental program was implemented, in an attempt to optimize process parameters. Temperatures ranging from -5 C to 160 C were used for drying with a variety of solvents at both ambient pressure and under vacuum conditions. Drying times varied from weeks to several months. The use of formamide as a drying control chemical additive helped reduce shrinkage and warping, and eliminate fragmentation, and the addition of butanediols and acrysol resins for cross-linking resulted in strengthening of the gels. Transmission characteristics improved with lower water: ester molar ratios in the alcogel composition. Limitations of the process at this stage include the measurable shrinkage of the samples (typically 50%) and long drying times. Although significant improvements to the process were realized, further research is required to develop it to the point of commercialization. Logical postulations for further improvements were developed, and would provide an excellent starting point for future, and hopefully final, commercial development.

## EXECUTIVE SUMMARY

Aerogel is an extremely light, porous, material which has a very low thermal conductivity. In transparent form, it has excellent potential as a superinsulating filler for window systems. The main obstacle to this application is that the traditional method of aerogel production requires venting solvent from an alcogel in an autoclave at supercritical temperatures and pressures. Increasing interest in energy conservation has sparked recent development of improved production methods, with most work concentrating on refining autoclave production techniques. This project explored an alternative production method which employs freeze drying of alcogels rather than supercritical production. The work was based on the results of the contractor's previous NRC sponsored basic research on this subject, which led to characterization of the basic process. The objective of this project was to develop the process and demonstrate the fundamental basis of a commercially viable technique for the production of porous transparent aerogel superwindows.

A rigorous experimental program was implemented which involved the preparation of dozens of alcogel samples of varying compositions. The main process variables which were studied include:

1. variation of the primary reactant
2. variation of the primary catalysts
3. variation of TEOS:$H_2O$ molar ratio
4. crosslinking with butanediols and later with acrysol resins
5. addition of drying control chemical additive

6. variation of the mutual solvent
7. solvent exchange of the mutual solvent
8. testing of various drying methods

The density, porosity, and optical transmittance of most of the samples were measured. Thermal conductivity testing was conducted on a limited number of samples.

Although improvements to the process were realized, they were not as pronounced as had been anticipated. Main observations include:

1. A [TEOS]:[$H_2O$] molar ratio close to 1:4 improves optical transmittance in the visible region.
2. Addition of a Drying Control Chemical Additive such as formamide helps reduce fragmentation.
3. Addition of crosslinking agents strengthens the gel and reduces fragmentation - 1,3-butanediol was the best of the agents tested. Samples prepared with acrysol resins near the end of the project are not yet completely dry, but also appear to be effective. Shrinkage of these samples is approximately 10% less than samples prepared previously, but only one is dry after seven months. Photographs of these samples are included in Figures 34 and 35 of Appendix I.
4. Controlled evaporation at a slow rate with a flowing atmosphere of air produced the best samples with the least cracks.

Excessive shrinkage and long drying times continue to be a problem. The drying time was ultimately reduced to 8 - 10 weeks for air drying at room temperature and atmospheric pressure.

Shrinkage was typically 50 - 60% for t-butanol exchanged gels, and 40% for pinacol and phenol exchanged gels. The gels prepared with acrysol resin crosslinking agents exhibit reduced shrinkage to date, but are not yet dry enough to draw any conclusions. The protracted drying times and excessive shrinkage render further development necessary to conclusively prove the process commercially viable.

Postulations for further improvements were identified during the course of the project, and would provide an excellent starting point for subsequent development. Main recommendations include:

1. Attempt to reduce the drying time by increasing the rate of diffusion of the solvent in the alcogel. This might be accomplished by repeatedly subjecting the sample to two unique temperatures, one above the M.P. of the solvent and the other below.
2. Determine the mechanism of shrinkage.
3. Prepare samples with ether as the mutual solvent, since ether has a low surface tension.
4. Continue evaluation of acrysol resins as cross-linking agents by further variation of the reaction parameters.
5. Prepare samples with surfactant added to the initial preparation to determine if it reduces fragmentation.

Overall, the project was a qualified success, since process improvements were realized. However, further development is required before commercial implementation can be achieved. While recent improvements to autoclave production methods have made them more economical, the flexibility of the freeze drying method

still suggests an overall production advantage. Consequently, in light of recent efforts to commercialize aerogel autoclave production, further financial support for the development of the freeze drying process is warranted.

## 1.0 INTRODUCTION

Aerogels are extremely light (density as low as .02 gram per cubic cm), porous materials consisting of inorganic oxides or mixtures of oxides such as silica, alumina, zirconia, stannic or tungsten oxide. Their extremely low thermal conductivity (nominally 10 mW/m.K) and low thermal loss co-efficients, (nominally 0.5 $W/m^2.K$ for a 15 mm thick layer) coupled with the fact that they can be translucent or transparent, give silica aerogels the potential to be ideal superinsulating fillers in window systems.

Aerogels are transparent because their pores are much smaller than the wavelength of light; therefore they transmit rather than scatter light. Insulating values are high because of the high ratio of void volume to volume of solid matrix, and the extremely small pore size.

To date, aerogels have been produced primarily in the laboratory, with some small scale production for specialized applications such as Cerenkov radiation detectors. There are two main obstacles hindering commercialization of this material. First, methods need to be developed to improve physical and optical properties to the point of commercial acceptability. Areas of concern include:

i) most aerogels produced so far have some slight, but noticeable colour effects resulting almost exclusively from light scattering.[11] Aerogels have a slight bluish appearance when viewed against a dark background and cause a slight reddening of transmitted light. It is anticipated that these effects can be minimized.

ii) Porous materials are extremely susceptible to liquid and/or absorption. Aerogel filled windows must therefore be sealed from the environment to prevent clouding and optical degradation. Evaluation and development of adequate sealing methods has yet to be fully addressed.

Aerogels are also relatively fragile and can be crumbled quite easily. They are significantly stronger in compression than in tension or sheer, however, which is compatible with glazing filler applications.

The second problem slowing commercialization of aerogels is the need to develop preparation techniques that are more suitable to mass production than the autoclave method commonly used in the laboratory. This was the main objective of this project.

The usual method of production of silica aerogels starts with the controlled conversion of a sol into a gel i.e.:

i) The growth of clusters or polymer chains from a chemical solution, generally an alkoxide.

ii) The crosslinking of these primary entities and the formation of a coherent network of silicon and oxygen atoms - still intact.

Initially, tetramethoxy silane (TMOS) is dissolved in methanol and reacted with water (hydrolysis) by adding a controlled amount of water. The resulting gel, called an alcogel, is directly dried in an autoclave under supercritical conditions (temperature: 239.4 C and pressure: 80.0 bars). The final porous product, the aerogel, can be obtained in a few hours. Supercritical conditions can be reduced to 40 C and 80 bars if carbon dioxide is used. However, the use of an autoclave is a major drawback for commercial production of aerogels - the autoclave required to maintain the fluid at high pressure is expensive to buy/build and operate. Production flexibility also would be limited by autoclave size. For these reasons NRC awarded the contractor a research contract in 1984-85, with a mandate to investigate innovative alternatives to autoclave aerogel preparation. A procedure was ultimately formulated which employs solvents to freeze dry cross-linked gels at low temperature and pressure.

Regardless of the production method used, the liquid solvent in the gel must eventually be replaced with air. Attempts to drive off the solvent by heating or drying result in the formation of liquid-vapour interfaces within the gel network. Because of the

very small size of the pores, surface tension effects between the gas and the liquid are very large, and cause considerable shrinkage due to partial collapse of the gel network. This collapse ceases when the gel structure is strong enough to withstand the high tensile strength of the liquid. The resulting hard glassy masses, called Xerogels, remain porous. To produce an aerogel, it is necessary to replace the liquid with air, without allowing the surface of the liquid to recede within the gel. If liquid is held under pressure greater than its vapour pressure, and the temperature is raised, it will be transformed into a gas at the critical pressure, without two phases having been present simultaneously. It is possible to slowly expand the supercritical fluid and obtain an air filled gel structure. This is the theory behind the autoclave method. An alternative is to allow the fluid in the pores of the gel to evaporate solid phase, i.e. freeze dry. This could reduce the interfacial tension within the pores, and the gel could dry without the collapse of its network structure. This method was researched under the Contractor's NRC research contract. Results were encouraging and prompted continued development under EMR sponsorship.

The literature on aerogels has been reviewed extensively up to the end of 1987 and the final review, presented in Appendix II, contains more than 200 references. Although aerogel formation has been widely studied, much attention has been focused on

fusing the gel to glass at much lower temperatures than required for manufacturing glass from the melt. The material thus formed usually have a high bulk-density (about 1.5 $g/cm^3$) compared to the desired values for window insulation of about 0.5 $g/cm^3$. Other groups have studied autoclave production of aerogels, but little effort has been focused on the freeze-drying method.

## 2.0 OBJECTIVES

The objective of this project was to develop and demonstrate the fundamental basis of a commercially viable process for the production of porous transparent aerogel superwindows. The work was based on the results of the contractors' previous basic research in this field, and concentrates on the freeze drying preparation of cross-linked gels.[12]

## 3.0 METHODS AND RESULTS

### 3.1 Logic of the Experimental Program

The original work plan was summarized in the proposal for this contract and was based on recommendations made by the project team during their previous basic research. The suggested program for development of the freeze dried process was as follows:

1. Develop and refine basic silica ($SiO_2$) procedure previously researched, with the objective of producing large monolithic aerogel samples.
2. Investigate alternative gel solvents.
3. Investigate microwave drying of samples at the tertiary stage.
4. Investigate improved methods of cross-linking.
5. Optimize preparation alternatives and prepare prototype super window samples.
6. Determine salient properties of prototype samples.
7. Evaluate commercial viability, cost effectiveness, and define terms of reference for commercial implementation.

The experimental program was elaborated at the start of the project, as summarized in Figure 1. As the samples dried and data was collected, the program was modified in response to observed results. Modifications were kept to a minimum, but results of each stage of the program were not always as conclusive as hoped. Long range scheduling of the program was difficult since drying times varied considerably with

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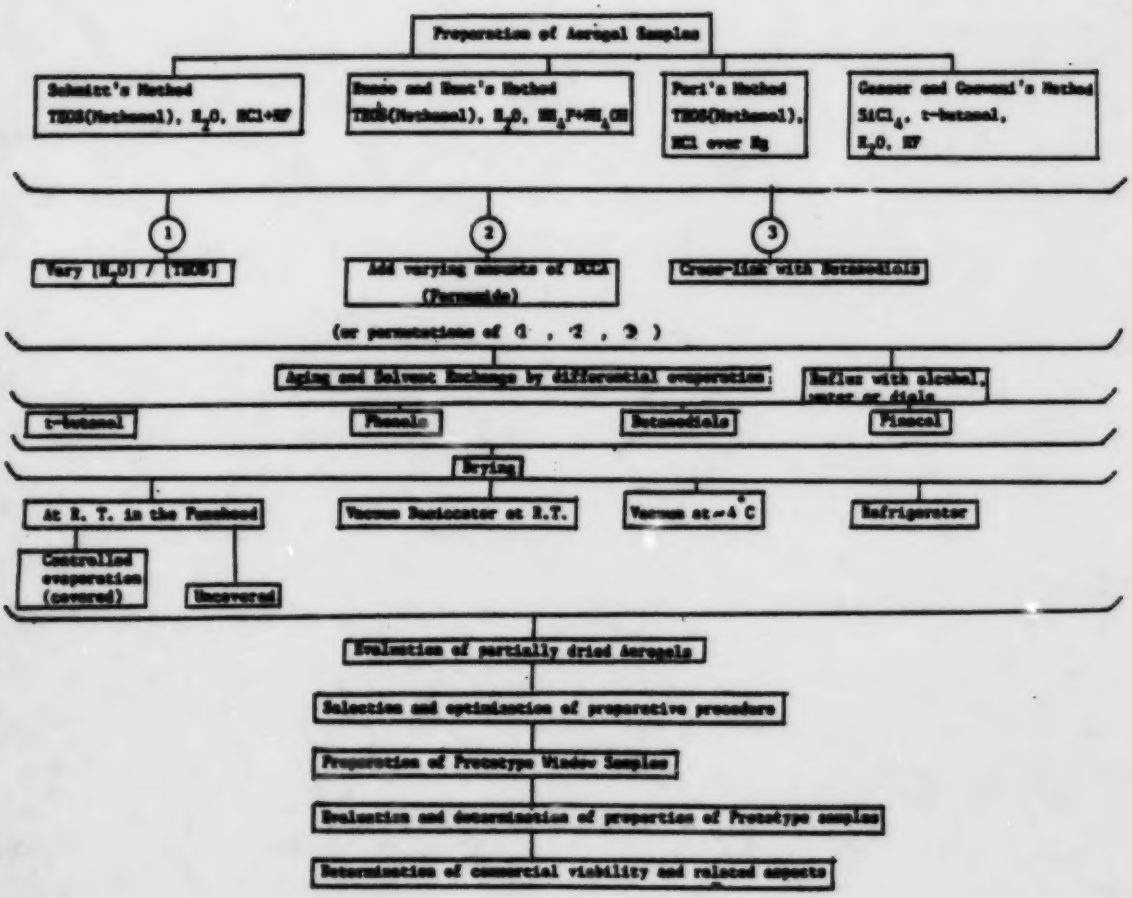
Figure 1: Experimental Program



variations of process parameters.

The actual experimental program is summarized below. Overall, the original schedule was followed quite closely, with some additions to its scope. The details of each phase, and corresponding key observations, are discussed in the next section. Although the process variables studied are presented individually, the corresponding experiments did not necessarily occur in the order listed. Experiments which focused on different variables were often conducted in parallel, and a certain amount of back-tracking, or repeating a group of experiments in greater detail, was required.

## 1.0 PRELIMINARY EXPERIMENTS

1.1 Gel formation with TEOS, TMOS or $SiCl_4$ used as the reactant, plus preparation by Peri's method. Peri's method involves preparation of TEOS gels with a HCl catalyst, and subsequent gelation on a bed of mercury.

**Objective:** See 1.1.1

1.1.1 Variation of Catalysts

Primary catalysts used were HCl and HF (acid) and $NH_4F$ and $NH_4OH$ (base).

**Objective:** To establish the best process with respect to the kinetics of the process (drying times), fragmentation and shrinkage.

1.1.2 Variation of TEOS: $H_2O$ molar ratio (TEOS gels only)

**Objective:** Transparency varies with this ratio. Experiments determined to what extent and established acceptable limits for this application.

1.1.3 Crosslinking with Butanediols

**Objective:** To determine whether crosslinking strengthened the gel, improved texture or retarded fragmentation, and to what degree.

1.1.4 Varying amounts of Drying Control Chemical Additive (DCCA)

**Objective:** To test whether addition of DCCA relieved the drying stress and reduced cracking.

1.1.5 Variation of the Mutual Solvent

This was an addition to the initial program outlined in Figure 1.

**Objective:** To determine whether the solvent exchange process could be deleted from the overall process, by preparing the gel in solvents normally used for solvent exchange directly.

1.1.6 Solvent Exchange of the Mutual Solvent

**Objective:** The different mutual solvents used all have different freezing and melting points, different surface tensions and different vapour pressures. Most of them have melting points which are higher than that of

methanol. The experiments studied the effect of different solvents on drying time, shrinkage and cracking.

1.2 General

The methods listed in section 1.1 were used to prepare many samples, with variations of the process parameters as listed in sections 1.1.1 through 1.1.6.
In some cases, more than one parameter was studied in parallel. This is reflected by the number and variety of samples prepared.

## 2.0 TESTING OF DIFFERENT DRYING METHODS

Varying degrees of controlled evaporation were used to dry the aerogel samples. Variables included drying temperature, air flow rate, and composition of the flowing atmosphere.

**Objective:** To study the effect of drying conditions on sample properties, primarily drying time and fragmentation.

## 3.0 SELECTION AND OPTIMIZATION OF THE MOST PROMISING METHOD

Two of the TEOS preparations were chosen as the most promising, and further efforts concentrated on their development. The process parameters identified in section 1.1 were studied in greater detail, and larger samples were prepared. The relative ambunt of orthosilicate to water was increased in an attempt to

increase transparency.

## 4.0 ADDITIONAL VARIATIONS

The following experiments were not identified in the original experimental program since they were initiated in response to information obtained during project implementation.

### 4.1 Avnir and Kaufman's Method

In November, 1987, the researchers reviewed a paper published by Avnir and Kaufman, which described a method of obtaining gel without a mutual solvent. Xerogel samples were subsequently prepared by this method, and their properties compared to the other aerogel samples.

### 4.2 Addition of Glycerol

Also in November, 1987, a paper by Wolfrum was reviewed which reported the preparation of crack-free monolithic $Al_2O_3$ gels with 1% glycerol added to the sol. Samples were prepared with glycerol to determine its effect.

### 4.3 Acrysol Resins for Crosslinking

In December, 1987, the project team learned of a range of water soluble resins which could be used in place of butanediols for crosslinking. Acrysol W5-24, W5-32 and W5-50 resins were donated to the project in February by the manufacturer, Rohm and Haas. Samples were prepared to see if resins would improve their strength and reduce fragmentation.

## 3.2 DETAILED PROCEDURE AND KEY RESULTS

### 3.2.1 Preliminary Experiments

#### 3.2.1.1 Gel formation with tetraethylorthosilicate (TEOS)

**A. Variation of [TEOS]/[$H_2O$] molar ratio.**

Several samples of silica alcogels were prepared using different molar ratios of TEOS and water, with varying amounts of methanol used as the mutual solvent.

$$Si(OC_2H_5)_4 + 4H_2O \xrightarrow[\text{methanol}]{\text{catalyst}} Si(OH)_4 + 4C_2H_5OH \quad (1)$$

$$n\ Si(OH)_4 \longrightarrow n\ SiO_2 + 2nH_2O \longrightarrow \text{Silica Alcogel} \quad (2)$$

The mole ratio of TEOS to water was varied from 1:4.5 to 1:18. The transparency of the gel decreased with the increase of this ratio. The first batch followed Schmitt's method, using HCl (0.5 ml) and HF (1.0 ml) as catalysts, with molar ratios of TEOS to methanol varying from 1:8 to 1:32. The setting time of these gels varied from 5 to 20 minutes. All the gels were transparent. After the gels had set in the molds, which were mostly 9cm x 0.15 cm Pyrex petri dishes, methanol was added to the wet gel to keep the surface from drying. Tertiary butanol was then added in sufficient amounts (liquid volume was equal to the volume of the gel) to facilitate the exchange with methanol. The methanol slowly evaporated, thereby leaving the t-butanol in the pores of the gel. The gels were then cut into pieces and subjected to different freeze drying conditions.

**B. Variation of Catalysts**

Different batches of alcogels were prepared with different catalysts, specifically $NH_4F$ and $NH_4OH$ (pH = 8, 10)[2], and HCl (pH = 6). TMOS gels were also prepared in the absence of any catalyst. In an earlier experiment it was found that pre-cooling the solutions to 0 C was essential for proper gelling with $NH_4OH$ catalysts. With $NH_4F$, HF and $NH_4OH$ (pH = 8) gelation time was 20 - 30 minutes. With HCl (pH = 6) catalysts, as long as 7 - 10 days were required to form a gel, and these gels were softer than the base catalyzed gels. The base catalyzed gels exhibited less shrinkage and fragmentation than the acid-catalyzed gels.

**C. Cross-linking with Butanediols**

Cross-linkage improves and strengthens the gel formation from alkoxides. Diols are good cross-linking agents, and three butanediols, 1,3-, 1,4- and 2,3- were added to the samples. The diols were generally added to the hydrolyzing solution from the beginning, with care taken to maintain homogeneity. The solution was allowed to gel at ambient temperature and pressure. The gels appeared to have better texture and less shrinkage. They were then solvent exchanged and freeze-dried, but drying was slow.

**D. Use of Formamide as a Drying Control Chemical Additive (DCCA)**

It has been found recently that organic drying control chemical additives (DCCA) such as formamide, $HCONH_2$ can relieve the drying stress and thereby reduce or eliminate cracking and

fragmentation.[3]

Several samples were prepared by adding formamide in varying concentrations to the alkoxide solution (TEOS, methanol, butanediol, $NH_4$, $HF/NH_4OH$). In all cases there was a noticeable decrease in the extent of cracking. Drying time was, however, increased for each of the samples.

**E. Variation of the Mutual Solvent**

The initial samples of alcogels were prepared with methanol as the mutual solvent. Although methanol turned out to be the preferred option, experiments were done later with t-butanol, phenol and pinacol as the mutual solvent. The samples prepared with t-butanol (t = 23 C) turned opaque during the initial process of ageing and drying, but those prepared in molten phenol (t = 45 C) and pinacol (t = 45 C) were initially transparent. The sample prepared in phenol turned opaque during the final drying stage (165 C), and had only two cracks. The large pieces withstood pyrolysis at 500 C without any cracks developing, but the final product, though porous and of low density, was opaque, very fragile and chalk-like in appearance. The sample prepared in pinacol also turned opaque much later in the drying stage and subsequently crumbled into tiny particles. A sample prepared with 50% methanol-ether mixture as the mutual solvent showed promise. The sample was aged in ether for three days, then solvent exchanged with ether by decantation 6 times, and finally left immersed in ether. Ether was then removed by evaporation

while the sample was kept covered with Saran Wrap. The sample remained monolithic until the cover was lifted, which initiated one large crack. Since ether has low surface tension, the interfacial tension during its evaporation from the capillary pores of the alcogel is considerably reduced, thereby reducing drying stresses.

An important observation for this sample was that several cracks, which developed while decanting the ether, were annealed when the sample was subsequently submerged in ether and then finally allowed to dry.

**F. Solvent Exchange**

The mutual solvent used in the preparation of alcogels and the alcohol generated during hydrolysis were exchanged with higher melting solvents. The four solvents used were t-butanol, 1,4 - butanediol, phenol and pinacol, $(CH_3)_2C - \overset{OH}{\overset{|}{C}} - \overset{OH}{\overset{|}{C}} - (CH_3)_2$. The general procedure was to add a volume of solvent equal to that of the gel, decant it off, and then replace it with a fresh solvent. The process was repeated at least four times. The gel was aged in the solvent it would be exchanged with for a least 24 hours, in order to strengthen it. Solvent exchange was accelerated by differential evaporation resulting from slow to moderate heating in a steam bath. Care was taken to keep the surface of the gel covered with the solvent in order to prevent crack formation. Differential evaporation was continued for a minimum of four

hours in each case.

### 3.2.1.2 Other methods of gel preparation.

#### A. Peri's Method

Two sets of gels were prepared following Peri's method.[4] The prepared gels were flat, hard and transparent. The alcogels were solvent exchanged with t-butanol and later freeze-dried under the fume-hood. All the gels developed many cracks, broke into many pieces, and were not considered promising.

#### B. Gel Preparations using $SiCl_4$, butanediols and t-butanol.

i) t-butanol as the mutual solvent

Gels were prepared by hydrolizing TEOS in t-butanol instead of in methanol. $NH_4F$, HF in $NH_4OH$ (pH = 10) was used as the catalyst. After aging in t-butanol for a day, the alcogel was further solvent exchanged with t-butanol by differential evaporation. The gel was opaque due to crystallization of t-butanol throughout the gel matrix. The gels cracked into small pieces which crumbled on holding. Clearly this method did not appear promising.

ii) Gels made with $SiCl_4$ and t - butanol

t-butanol was added in excess to $SiCl_4$ to produce $Si(OC_4H_9)_4$, which was hydrolyzed using HF as a catalyst. After aging for one day in t-butanol, the gel was solvent exchanged with t-butanol. The gels were an opaque white,

similar to those prepared from TEOS in t-butanol, and crumbled to pieces during freeze drying. This method obviously did not hold any promise. Gels prepared in an ice-water bath also produced similar results. Some gels dissolved during aging or differential evaporation and addition of 1,4-butanediol did not improve the samples.

iii) Gels made with $SiCl_4$, 1,3- or 1,4-butanediol in methanol at 0 C

Another variation of the gel comprised a solution of TEOS in methanol and water at 0 C, added to a well stirred solution of $SiCl_4$ and 1,4- or 1,3-butanediol in methanol. The solution was placed in an ice-water bath. Gelation occurred in 48 hours and the gel was aged in methanol and 1,4- (or 1,3-) butanediol for two days. The alcohols were removed by differential evaporation. The gels were clear and rubbery and some had a yellowish tint. The gels could be cut into pieces but did not dry fast. They finally proved to be less promising than they were initially thought to be.

**3.2.1.3 Drying Methods**

**A. Terms Used to Describe Alcogel Drying**

To clarify the description of the alcogel drying process the following terms are defined:

i) Observed porosity:

When one's wetted finger sticks to a gel sample, the

sample is observed as porous.

ii) Primary Drying Stage:

When a gel sample is wet and perspiring with solvent, drying is in the primary drying stage.

iii) Secondary Drying Stage:

When a gel sample is no longer wet or perspiring with solvent, but does not exhibit observed porosity, the sample is in the secondary drying phase.

iv) Tertiary Drying Stage:

When a sample exhibits observed porosity but is still losing mass due to solvent evaporation. At the end of this stage the sample no longer loses significant mass by solvent evaporation, and will be either a xerogel or an aerogel, depending on the structural integrity of the silica matrix.

**B. Various Drying Routines**

Based on previous experience, the rate and method of drying has significant impact on the properties of the sample. Varying degrees of controlled evaporation were studied. Rapid evaporation invariably led to serious fragmentation of the gel. The various routines evolved during the initial experimentation, and are briefly described below.

1. Controlled Evaporation

i) After solvent exchange, the wet gel was cut into small pieces and transferred onto a mesh located inside

partially covered plastic petri dishes. The dishes were later stored in (1) a freezer, (2) a refrigerator, (3) a water cooler (T = 4 C) with the space above the gels continuously evacuated by a mechanical vacuum pump or (4) a vacuum desiccator (RT, 22 C).

The results of low temperature drying were not promising. In most cases, the solvent crystallized throughout the matrix leading to the complete collapse of the gel matrix. Samples stored in the water cooler dried very slowly, and were still not dry after eight months. Samples stored in the vacuum desiccator dried in 4 - 5 months but were severely fragmented.

ii) Room Temperature and Atmospheric Pressure

Gel samples dried at room temperature (22 C) were placed on wire mesh inside plastic petri dishes, which were both covered or uncovered, and placed in the fumehood. Some gels kept in covered dishes did not suffer any fragmentation and required 8 - 16 weeks drying time. Most of the gels kept in uncovered dishes suffered more fragmentation, but some, especially the ones prepared with the addition of formamide and 1,3-butanediol, did not experience fragmentation or cracking. The gels prepared with 1,4-butanediol as a cross-linking agent fragmented more than those prepared with 1,3-butanediol. The gels remained transparent during most of the drying period,

becoming cloudy in the last stage only. In a few cases slight warpage developed if the gel was dried relatively quickly in an uncovered dish.

iii) High Temperature

Controlled evaporation at high temperature was tried for phenol exchanged gel samples and the gels prepared with phenol as the mutual solvent. The alcogels, which were initially freeze dried at room temperature until shrinkage ceased, were placed on mesh in Pyrex petri dishes and kept in a variable temperature vacuum oven which was continuously evacuated. The samples were dried at 60 C for the first 6 hours, 90 C for the next 12 - 20 hours, and finally at 160 C for 4 - 8 days. When the samples looked dry, they were transferred to a muffle furnace where they were held at a temperature of 300 C for 12 hours. The samples turned black. They were then pyrolyzed at 500 C in air to oxidize the residue. The phenol exchanged samples became transparent (or translucent), but those prepared in phenol turned opaque.

The other t-butanol and pinacol exchanged transparent samples were placed in an oven at 90 C for 12 hours after the last stage of drying (i.e. when they become slightly opaque/misty). They clouded temporarily, but later regained their transparency. There was no observable shrinkage caused by this heat treatment. A nominal

improvement in transparency of 10-20% was realized during subsequent pyrolyzing of the dry aerogels (Appendix I, Figure 1A, 1B - 4A, 4B).

iv) Drying in a flowing atmosphere of $CO_2$ and air.
Another hypothesis tested was that drying might be accelerated if the vapour above the alcogel could be swept out by a heavy inert gas such as $CO_2$ or air. An apparatus was constructed which allowed compressed air or $CO_2$ to flow through a sealed tray which contained the alcogel samples. The drying rate initially appeared to be faster, but later levelled off so that this method proved to have little benefit over drying in the fumehood.

A second apparatus was used to test drying in a flowing atmosphere. The samples were placed inside covered petri dishes which were set on a platform inside a loosely covered box. Compressed air was introduced to the box from beneath the platform. The air flow rate was too high, causing the samples to warp and crack. A slower flow rate (approximately 3.0 litre/min) would probably yield better results.

A persistent problem has been difficulty lifting the wet alcogels on to the mesh in the plastic petri dishes for drying. The gels frequently broke during this operation. Two solutions were tested. The first was to coat the

glass molds with vaseline. The alcogels were set directly on the vaseline lined molds for freeze drying. This method appears to be promising in the sense that many samples remained free of cracks and drying progressed smoothly until the lid of the moulds were lifted. Most samples suffered one crack. The second method tried was to invert the covered petri dish during the start of the primary drying stage, when the alcogel is just slightly dry, so that the sample would gently fall onto a pad of cotton wool and expose the other side to air. Attempting to free the gel too quickly, or by force, could aggravate the interfacial forces and induce cracking. To date, both methods have shown variable success.

### 3.2.2 Selection and Optimization of Promising Preparations

After the initial experiments, an evaluation of results identified the most promising gels in terms of physical properties. (i.e. strength, warpage, cracks, density, shrinkage, and transparency). Further efforts therefore concentrated on the following preparations:

**Method 1**

**TEOS, methanol, formamide, 1,3-butanediol, and water with catalysts:**

i) HCl (pH = 6)

ii) $NH_4F$, HF in $NH_4OH$ (pH = 8)

and solvent exchanged with

i) t-butanol

ii) phenol

iii) pinacol

**Method 2**

TEOS, phenol, formamide, 1,3-butanediol and water with catalysts i) HCl (pH = 6) and ii) $NH_4F$, HF in $NH_4OH$ (pH = 8).

Cross-linking agent 1,4-butanediol was not as successful as 1,3-butanediol. The matrix of some of the gels prepared with 1,4-butanediol collapsed or dissolved during the solvent exchange process.

Shrinkage was noticeably less for methods 1 and 2 above when pinacol was used for solvent exchange. Cracking was also minimized and lower material density was achieved.

The base catalyzed samples were strongest, and samples prepared by method 1 were of superior optical quality. Some samples prepared by method 1 with acid (pH = 6) catalysts took as long as two weeks to gel, and the resulting gel was softer than those obtained by base-catalysis.

### 3.2.3 Additional Variations

At this time, a paper by Avnir and Kaufman was published which described a method of obtaining gel without a mutual solvent. The alcohol released during the hydrolysis of TMOS or TEOS is

sufficient to convert the bi-phasic system into a homogeneous phase, resulting in a transparent xerogel. Gels prepared by this method under neutral conditions were transparent, air dried in three weeks, and had very few cracks. Their optical quality was much better than other samples prepared so far. However, the density of these xerogels, was quite high, 1.5 to 1.8 $g/cm^3$. Similar preparations of xerogels using TEOS were not promising. The solution remained biphasic for a long time, even under acidic conditions (pH = 6). An opaque gel formed within 48 hours but a transparent phase remained which required 2 - 3 weeks to gel. The opaque gel developed cracks during aging.

Some gels were also prepared by the hydrolysis of TEOS and TMOS in the presence of 1% glycerol, in the hope that this would reduce cracking. However, the gels developed cracks after air drying and later shattered into strong, transparent pieces.

### 3.2.4 Evaluation of Physical Properties

#### A. Density

Densities were determined for the dry aerogel pieces. An Ott planimeter (Type 16) was used to measure the area of each sample, and slide-calipers were used to measure their thickness. The sample volume could then be calculated, its weight measured and the density evaluated within approximately 10% accuracy (Table 3).

#### B. Porosity

After the bulk density of an aerogel sample has been determined,

its porosity, , can be calculated (Table 3) using the following formula[1]:

$$\varepsilon = \frac{\rho_{bulk} - \rho_{SiO_2}}{\rho_{air} - \rho_{SiO_2}}$$

(Density of amorphous $SiO_2$ = 2.2 g/cm$^3$ and density of dry air at 25 C and 745 mm Hg = 0.001160 g/cm$^3$)

**C. Optical Transmission**

Optical transmittance of the dry aerogel pieces was measured in the 400 - 800 nm spectral range with a Hewlett Packard 8452A diode array UV-visible spectrophotometer. The spectral traces are attached as Appendix I. (See also Table 2). Although transmission as high as 70% at 800 nm was achieved for some aerogel samples, their transmission was generally lower than that of the xerogel samples. The aerogel samples prepared with a [TEOS]/[$H_2O$] ratio of 1:4 are expected to exhibit improved transmission characteristics, but they are not yet dry. (12 weeks).

**D. Thermal Conductivity**

Thermal tests were conducted by the Mechanical Engineering Department of the University of Manitoba. The apparatus used is designed to measure the thermal conductivity of solids according to ASTM Standards. The temperature gradient resulting through a brass tube, with and without the presence of the sample, upon application of a specified heat input is measured. The ratio of

the two gradients is used to determine thermal conductivity. Due to difficulties with the test apparatus, testing was delayed. The tests are now complete, but the results will not be available until October 4, 1988. They will be forwarded as an addendum to this report.

### 3.2.5 Preparation of Samples of Larger Dimensions

Large Pyrex petri dish molds (150 cm x 1.5 cm) were used to prepare larger samples. Both TEOS and TMOS hydrolysis were used, and method 1 Section 3.2.4 was followed using basic catalysts. For most of these samples, the molds were coated with vaseline. Samples were solvent exchanged four times with t-butanol or pinacol and underwent repeated decantation and renewal after the initial ageing period of at least 3 - 4 days. These large samples are presently in the secondary stage of drying.

### 3.2.6 Gels Prepared with Various Acrysol Resins as Cross-Linking Agents

One innovation introduced during the execution of this project was to introduce 1,3-butanediol as a cross-linking agent to strengthen the gel. It was brought to our attention that Rohm and Haas produced a range of water-soluble resins which could also act as cross-linking agents. Acrysol WS-24, W5-32 and W5-50 resins were obtained through the courtesy of Rohm and Haas. Gels prepared with the addition of Acrysol WS-24, with a resultant concentration of 15%, became opaque during ageing and drying and finally developed cracks. However, dilute solutions of 2% (resultant concentration 0.60%) resulted in transparent gels

which did not crack for a long time. Most samples experienced one crack when the lid of the petri dish was lifted. Since all samples experienced the same phenomenon, the cracks can be directly attributable to the drying procedure. The gels were stored in vaseline lined Pyrex petri dish molds & were solvent exchanged with pinacol. At present, these gels are in the secondary stage of drying. One of the samples is ready for pyrolysis at high temperature, but the rest are not dry. Drying time to date has been seven months. These samples exhibit slightly reduced shrinkage, approximately 10% less than most previous efforts, but shrinkage is still nominally 40%. Two of the samples prepared with acrysol resins have only shrank by about 25% to date, but they are not completely dry. Photographs of these samples, and those described in Section 3.2.5 are shown in Figs. 34 and 35.

### 3.3 Summary of Results

After preparing several dozens of alcogel samples from hydrolysis of TEOS, which is less toxic than TMOS, and varying the [TEOS]/[$H_2O$] ratio, mutual solvents, catalysts, cross-linking agents and drying control chemical additives, it was possible to select the most promising combinations in terms of improved monolithicity, optical transparency and porosity. The following phenomena were observed:

1. [TEOS]/[$H_2O$] ratio close to 1:4 enhances optical transmittance characteristics in the visible region.

2. The use of formamide, $HCONH_2$, relieves the drying stress and thus inhibits fragmentation of the gels.
3. Butanediols (especially 1,3-butanediol) used as cross-linking agents strengthen the gel.
4. The rate of drying a gel has significant impact on the initiation of cracking. The best method used, which produced monolithic samples, was drying of the gel in a covered Pyrex mold which had been lined with vaseline and housed in a flowing atmosphere of air. The drying rate must be slow. Two samples, 870722/K-B (Dup) (7.5 cm dia x 0.5 cm) and 871214/2 (3.5 cm dia x 0.25 cm) remained monolithic until the end of the tertiary stage of drying. The latter sample did, however, eventually split into two pieces. (2/3 and 1/3 of the total area).
5. Acrysol WS-24, WS-32 and WS-50 resins in dilute concentrations (.002 - 3%) showed promise as cross-linking agents. The gels prepared with these reagents appear to be strong, monolithic, but translucent. The gels are in the secondary drying stage. The only cracks are directly attributable to a sudden change in drying conditions.
6. Among the catalysts tried, $NH_4F$, HF in $NH_4OH$ (pH = 8), produced gels with the best texture and optical quality.
7. The Xerogel prepared from TMOS without a mutual solvent dried within 3 weeks by air drying at room temperature and atmospheric pressure. The optical transmittance of the Xerogel sample was 70%, compared with 55% for other aerogels

dried so far. However, its density is high (1.8 g/cm$^3$).

8. The drying period for aerogels was reduced to 8 - 10 weeks for air drying at room temperature and atmospheric pressure.
9. Shrinkage was typically 50-60% for t-butanol exchanged gels, and 40% for pinacol and phenol exchanged gels.

### 3.4 Overall Project Implementation

This project is a prime example of the need for teamwork to achieve technology transfer. The interdisciplinary research team combined the academic expertise of the pure scientist with the pragmatism of the consulting engineer. Responsibilities were divided as follows:

Management, Engineering and Technology Transfer -

E. J. Faraci and Associates Ltd.

Scientific Investigation -

spdf Chemical Associates Ltd.

The project was administered through the Research Division of E. J. Faraci and Associates Ltd., under the direction of Mr. Gordon Shymko. The firm was responsible for overall project management and coordination, all contractual communications, plus engineering support. Specific duties performed in each of these areas are outlined below.

Management:

E. J. Faraci and Associates Ltd. was responsible for proposal preparation and submission, plus all related negotiations. Upon contract approval they assisted in structuring the overall

workplan, and scheduled semi-monthly project meetings and regular subcontract progress reporting. The firm prepared monthly progress reports and claims for submission to the Renewable Energy Branch of Energy, Mines and Resources Canada. The time spent by Mr. Shymko relaying information between the laboratory and the Scientific Authority was not insignificant.

Engineering:

Although spdf Chemical Associates Ltd. determined the technical direction of the project, E. J. Faraci and Associates Ltd. provided practical support to ensure that commercialization concerns were kept in mind when choosing between alternative experimental routes. Options were evaluated from the perspective of product performance and marketability as well as ease of fabrication, keeping in mind the fact that the preparation protocol is still in the preliminary phase of development.

The firm also coordinated measurement of the thermal properties of the aerogel samples. The Research Division performed the final commercialization evaluation and economic assessment which is summarized in this report. This involved investigating various production aspects of the project not addressed directly in the laboratory.

Technology Transfer:

The Research Division produced all of the monthly progress reports and the project proposal. It also edited and re-

formatted the technical sections of the final report and literature review, and supplied additional sections as required.

The management, engineering, and technology transfer functions described above are all necessary components of a successful project. They were deliberately segregated from the scientific investigation component with the enthusiastic endorsement of the technical expert, Mr. H. D. Gesser. The time required to carry-out the above functions is significant, and spdf Chemical Associates did not feel that performing these duties directly would be an effective application of their expertise. E. J. Faraci and Associates provided a necessary complement of skills and brought greater technical breadth to the project team. Although it is not necessary for many projects, depending on available resources and personnel interests/skills, the teamwork approach was deemed effective in this instance.

Scientific Authority:

Scientific and laboratory investigation was sub-contracted to spdf Chemical Associates Ltd. They were responsible for determining and implementing the experimental program and procedure, plus evaluating results and changing the focus of effort as required. They provided relevant conclusions and recommendations for further work. All of the aerogel samples were produced in the spdf laboratory.

## 4.0 COMMERCIALIZATION

### 4.1 Status of Aerogel Development

To date, aerogel production has been in limited quantities, and confined to the laboratory. The widest practical application of the material has been its use in Cerenkov radiation detectors. Two main groups have been involved with its production for this purpose: 1) Gunter Poelz and his co-workers at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg supplied a detector there with about 1,700 litres of silica aerogel, 2) Sten Henning and Guy V. Dardel at the University of Lund in Sweden generated about 1,000 litres of aerogel for an experiment at the European laboratory for particle physics (CERN). Both of these groups employed the autoclave method of drying. In 1984 the Swedish group had a methanol leak from their 3,000 litre autoclave into the building. An explosion ensued which destroyed the entire facility, and serves as an example of why the autoclave method is not ideal for mass production.[13]

A research group led by Arlon J. Hunt at the University of California at Berkeley has been developing techniques to produce porous transparent aerogels, and investigating their properties for insulating applications, since 1982. Two of the group's main achievements have been preparation of the gel from tetraethoxysilane (TEOS) instead of the poisonous tetramethoxysilane (TMOS), and substitution of carbon dioxide for the alcohol that is traditionally used as the fluid phase.

Carbon dioxide is nonexplosive and needs to be heated only above 31 C during drying. Both of these developments significantly improve the suitability of the process to mass production. The Berkeley approach to this research has very definitely been conducted from a commercialization and cost-effectiveness point of view. Patent rights for the $CO_2$ drying process have been transferred to Quantum Optics Company. One recent publication suggested that this company will start producing commercial quantities of aerogel in two to three years.[14]

The freeze drying method developed under this contract has the potential to remove all of the major problems associated with mass production of aerogels. Perhaps the greatest advantage it offers is complete flexibility regarding the size of the final windows, since this is no longer constrained by the size of the autoclave.

## 4.2 Proposed Markets

### 4.2.1 Present Markets

As mentioned in the previous section, the widest practical application of transparent aerogels to date has been their utilization in Cerenkov radiation detectors. No reason has been identified so far which would prevent the use of freeze dried aerogels for this application. However, this market is very limited, and cost competitiveness is not generally of primary importance. Although it might provide some additional income for a future aerogel production facility, this market is not large

enough to justify development of the freeze drying process.

The most promising application of aerogels which does warrant development of the freeze drying process, is use in insulating windows. The economics of this application are demonstrated in section 4.3, based on its ultimate goal of full size insulating windows for commercial and residential buildings. At present, the transparent properties of aerogels are not quite as good as those for glass, so aerogel glazings might never replace main picture windows. However, researchers are optimistic that the optical properties of aerogels can be improved to acceptable levels. One of the issues which must be addressed is determination of what are acceptable limits to optical performance for specific applications. Preliminary markets which would serve to both introduce and prove the technology include using aerogel windows as skylights, for glass walls and for small daylighting windows.

A third potential market for aerogel is its use to improve the efficiency of low temperature passive solar collectors. Present technology uses glass to protect the absorbing material. Approximately 40 percent of the energy absorbed is lost by conduction and re-radiation through the glass back to the atmosphere. The higher insulating values plus the low radiative transmission of aerogel at these temperatures would significantly reduce this loss. Consequently, this market also deserves primary consideration during the development of aerogel

production.

### 4.2.2 Future and Spin-Off Applications

Development of aerogels will almost certainly lead to new applications besides window insulation. It may be possible to tailor the material to provide a wide range of desired densities or indices of refraction. This would allow production of solid blocks which act as lenses or concentrators, and could be used for building construction, visually exciting architecture, or integral solar collectors. Aerogels may find a number of additional solar energy applications. Their use as insulating glazings for flat plate solar collectors has already been discussed. Another application might be thermal protection of a blackened house wall, designed to trap the heat provided by solar radiation. The wall would be covered with a black absorptive material that converts the sun's rays into heat. Because aerogel is a super insulator to the wall, most of the heat generated would penetrate the wall and enter the house rather than escaping to the outside. In summer a shade could be drawn over the absorber.

Extensive studies on the acous ic properties of aerogels have been carried out by a research group at W rzburg, Germany. Discussion of these studies is beyond the scope of this report, but one of the main observations is that aergoels have a low acoustic impedance, which is directly a result of the low sound velocity through the materials and its low density.

Consequently, aerogels could help to boost the efficiency of piezoelectric transducers, which are common components of cameras and of robotic systems that gauge distance by emitting ultrasonic waves.[13] This brief list of possible applications demonstrates that, as the material is better developed, more possibilities are likely to arise.

### 4.3 Potential Energy Savings

Replacement of conventional glazings with aerogel insulated windows is viable only if the value of the energy saved outweighs the added cost of production. The amount of energy saved is proportional to the location in question, with the greatest savings realized in areas which have colder climates. The energy saved can be estimated by the expression:

$q = U \Delta T$ ( 24 h/day), where

q = energy requirement, $kWh/m^2/yr$

U = overall heat transfer coefficient $W/m^2 .C$ ($U = 1/R$)

$\Delta T$ = heating requirement, C. days/year.

For a given application, $\Delta T$ = constant, and the energy saving resulting from the aerogel insulated window is $q = (U_c - U_a)\Delta T$, where the subscripts c = conventional, a = aerogel.

A typical value for T throughout much of Canada is 4982°C days/year. If an aerogel glazing with an RSI 1.75 rating replaces a double glazing window (RSI 0.35, R-2.0), the net

energy saving would be

$q = (0.5 - 0.1)$ Btu/h.ft$^2$.F x 5.6779 W/m$^2$.C/Btu/h.ft$^2$.F x
1 kW/1000 W x 4982 C days/year x 24 hrs/day

$= 340$ kWh/m$^2$/year

$= 31.6$ kWh/ft$^2$/year

Assuming natural gas is the energy source at $ 0.41/CCF and a fuel efficiency of 80%, the yearly cost saving is $ 5.95/m$^2$/year, or $ 0.55/ft$^2$/year.

If a five year simple payback is required to justify the investment, the maximum additional cost of an aerogel glazing would be $ 29.75/m$^2$ ($ 2.75/ft$^2$). The savings realized by replacement of a single glazed window would be slightly less than twice this amount, $ 53.42/m$^2$ ($ 4.96/ft$^2$) (RSI 0.17, R = 1.0). The cost saving would be higher if electricity was the heating source rather than natural gas. Based on the above assumptions, if a 1219 mm x 1830 mm (4 x 6 foot) window was required, the justifiable incremental cost of the aerogel over the single glazing would be $ 66.

A similar analysis could be performed for cooling loads in the summer.

Capture of radiative energy is also a factor influencing energy savings available from aerogel glazings. It is difficult to address this in a general sense, since the radiative performance

is extremely site sensitive. To obtain an accurate evaluation of the energy savings available, it is necessary to model the specific structure and simulate conditions on a yearly basis.

Although the study of the radiative heat transfer properties of aerogel was not included in the scope of work covered by this contract, other groups have investigated this area. The research group at Lawrence Berkeley Laboratory has reported that radiation heat transfer through aerogel is not a significant problem in the temperature range for insulating windows or transparent covers for low temperature passive solar collectors. It does, however, become a more critical factor at elevated (i.e. furnace applications) or greatly reduced (i.e. cryogenic) temperatures. They found that aerogel, in thicknesses greater than 1.0 mm, is opaque to infrared radiation between 7.5 and 40 m. At room temperature (e.g. for a conventional window application) the blackbody emission peak occurs around 10 m, well into this range, and for aerogel thicknesses of 0.5 - 5.0 cm, radiation heat transfer through an unmodified aerogel window is less than 15% of the total heat flux. For evacuated or high temperature furnace windows, this contribution can be over 50%.[15]

## 4.4 Production Considerations and Costs

### 4.4.1 Production Considerations

Aerogel production in the laboratory by the freeze drying method requires the following steps:

1. First a colloidal solution of silica is prepared. An ethyl or methyl silicate compound is mixed with an alcohol solvent and water, then catalyzed to form a colloidal suspension.
2. The colloid is poured into a mold and the silicate continues to hydrolyze until the gel is formed.
3. After setting, the gel is dried at room temperature at a controlled evaporation rate.

To estimate the cost of aerogel processing with any reasonable degree of accuracy would require conceptual design of the production facility. However, if it is clear that the process is easily adaptable to mass production, the cost component for the process can be minimized. This is where the advantages of an optimized freeze drying method are most noticeable. The mixing, cooling, and setting requirements can be easily adapted to mass production techniques. Drying would require space, but little equipment. The process could easily accommodate large or irregular size molds. The drying step of the autoclave method is clearly less adaptable to mass production. Even though the Lawrence Berkeley Laboratory group has reduced the supercritical drying requirements from 270 C and 115 bars pressure to 40 C and 80 bars by substituting the alcohol with liquid $CO_2$, the large autoclave required is still an item to build and operate. The problem is compounded by the fact that product size is limited by the size of the autoclave.

There are, however, major process concerns regarding the freeze drying method at its present stage of development. Shrinkage and long drying times are serious problems which must be overcome before the freeze drying method can conclusively offer any advantage over the traditional autoclave process. Aerogel prepared by the autoclave method experiences negligible shrinkage and can be dried in one day. To date, the best freeze dried samples exhibit about 40% shrinkage and require at least one week to dry. The project team is optimistic that these problems can be overcome with more development. Assuming they can, the process cost component should be minimized, and would be determined by the scale of the mass production facility. The material cost would be left as the major expense, as discussed in the next section.

### 4.4.2 Present Cost Projections

The freeze drying process developed under this contract is not considered to be optimized as yet. Therefore the amounts of each material required may change significantly for the final commercial preparation. At this stage of development the material cost for off-the-shelf chemicals required to produce an RSI-1.75, 13 mm thick aerogel slab in the laboratory is about $2161 per square metre ($200.83 per square foot)!. A breakdown of the material costs is given in Table 1.

**TABLE 1** **LABORATORY MATERIAL COSTS**

These costs are for sample 870722/k-B(Dup), and are considered typical at this stage of process development. The costs shown are for a 304.8mm x 304.8 x 12.7mm (1 ft x 1 ft x 1/2 inch) sample.

| CHEMICAL | LABORATORY PRICE (US $) | LABORATORY SAMPLE COST (US$) | BULK PRICE (CAN $) | MASS PRODUCTION MATERIAL COST (CAN $) |
|---|---|---|---|---|
| Formamide | 52.10/l | 96.78 | 1.47/l | 2.70 |
| t-butanol | 7.00/l | 42.84 | | Recovered |
| TEOS | 16.07/kg | 11.63 | 4.41/kg | 3.19 |
| Methanol | 4.38/l | 10.10 | | Recovered |
| HCl, catalyst | 20.00/l | 0.31 | | 0.31 |
| | | $ 160.66 | | $ 6.20 |

= $ 200.83 CAN

The material cost is dominated by the costs of formamide and t-butanol. It is anticipated that the amount of formamide can be reduced by a factor of two, pending proof by further experimentation. In an industrial process, virtually all of the t-butanol and methanol could be recovered by decantation followed by distillation. These efforts combined would reduce the cost to approximately $\$805/m^2$ ($\$74.79/ft^2$).

Perhaps most importantly, the cost of laboratory chemicals for research purposes should not be taken as representative of the mass production costs. An estimate of the bulk cost of the chemicals required was supplied by Harrison and Crossfield Ltd. These costs correspond to a product cost of $\$66/m^2$ ($\$6.20/ft^2$). It is almost certain that the cost of the chemical tetraethylorthosilicate will drop if a significant market develops, since the costs of the materials that go into the chemical are quite low.

The sample analyzed in Table 1 experienced 50% shrinkage during drying. Ultimately it is expected that a viable freeze dried process would involve little or no shrinkage. Assuming this can be achieved by addition of the correct solvent or cross-linking agent with negligible impact on cost, the materials listed in Table 1 would produce twice as much aerogel for the same mixture. Therefore the product cost would reduce to $\$33/m^2$ ($\$3.10/ft^2$).

Production costs by the Lawrence Berkeley Group were discussed in the December 1983 edition of Rodale's Practical Homeowner which states

> '...A year ago, Hunt put the material cost for a two-inch-thick R-10 window at about $10/square foot. He now has good reason to believe that the materials would cost closer to $2/square foot in even limited quantities...'

Adjusting for 3% inflation per year, and to Canadian dollars at today's exchange rate of $0.80 US/$1.00 Canadian, gives corresponding costs of $2.32 - $11.59/$ft^2$. For a 1/2 inch thick sample, these costs are only $0.58 - $2.90/$ft^2$, which is lower than the cost projected above. A 1982 report written by Arlon Hunt at Lawrence Berkeley Laboratory suggests that the estimated material cost is basically just the cost of the TEOS. Aerogels prepared by the freeze drying method will have the additional cost of the cross-linking agent, which can hopefully be reduced with further development. A future consideration must be the added cost of special purpose agents vs. the reduced production cost realized by the absence of the autoclave.

## 5.0 DISCUSSION

Significant improvements to the freeze drying method of aerogel preparation developed by the Contractors in 1985, were realized under this contract. Specifically:

i) Warpage was reduced so that samples are nearly flat.

ii) Fragmentation was greatly reduced.

Shrinkage remains a major problem, with most samples reducing to 50% of their original volume. Theoretically, if exact freeze drying conditions are achieved, there should be no liquid present within the gel pores, and therefore no meniscus, no surface tension, and no shrinkage. This suggests that exact freeze drying conditions are not being realized, and the exact nature of the present drying process is not fully understood. Further investigation of this phenomenon is necessary for full optimization of this process.

It is also necessary to reduce drying times by increasing the rate of diffusion of the solvent in the alcogel. This might be accomplished by repeatedly subjecting the sample to two unique temperatures, one above the M.P. of the solvent and the other below. If evaporation occurs only at the lower temperature, freeze drying may occur at a faster rate if diffusion of the solvent to the sample edges is accelerated by periodically maintaining the alcogel at the higher temperature for short intervals.

## 6.0 CONCLUSION

The freeze drying method developed for the preparation of silica aerogels by solvent exchange with higher melting solvents such as t-butanol, phenol and pinacol has potential. Pinacol and phenol exchanged samples produce aerogels of lower density. The drying period, however, must be reduced further to improve commercial viability.

The project objective was to develop and demonstrate the fundamental basis of a commercially viable process for the production of porous transparent aerogel super windows. Specific tasks required to achieve this objective were outlined in the project proposal, as follows:

1. Develop and refine basic silica ($SiO_2$) procedure previously researched with the objective of producing large monolithic aerogel samples.
2. Investigate alternative gel solvents.
3. Investigate microwave drying of samples at the tertiary stage.
4. Investigate improved methods of cross-linking.
5. Optimize preparation alternatives and prepare prototype superwindow samples.
6. Determine salient properties of prototype samples.
7. Evaluate commercial viability, cost effectiveness, and define terms of reference for commercial implementation.

Although each of these tasks except point three, investigation of microwave drying, was addressed, results were not as conclusive

as was hoped. Therefore, at this stage the process cannot be considered fully developed. The final samples are larger than any produced thus far, (approximately 60 cm in diameter, cm thick) but cannot be called large samples and are not adequate for prototype superwindows. Further effort is required to develop the process to the point of commercial viability. Significant improvements to the process were, however, developed under this contract, and definite theories for further improvements were clearly identified. They merely could not be tested within the scope and time constraints of the project. Overall, the project can be considered reasonably successful, and warrants continued financial support.

Major improvements in sample characteristics over those observed for samples prepared by this method during a previous research project include significantly reduced warpage and fragmentation. The two major areas which need more effort are: 1) determining what mechanism is causing the pronounced shrinkage of the samples, and 2) finding a way to reduce drying times to an acceptable duration. Shrinkage has a significant impact on the economics of aerogel production using the freeze drying method, whereas the drying time is more of a process concern.

Investigation of microwave drying of samples at the tertiary stage was not implemented since there were not enough representative samples dried to this stage to enable development of a proper experimental program.

## 7.0 RECOMMENDATIONS FOR FURTHER WORK

1. It is necessary to reduce drying times by increasing the rate of diffusion of the solvent in the alcogel. This might be accomplished by repeatedly subjecting the sample to two unique temperatures, one above the M.P. of the solvent and the other below, as discussed previously in Section 4.0.

2. The mechanism of shrinkage should be identified and the reason why exact freeze drying conditions are not being achieved should be investigated. The work outlined above may provide some clues in this area.

3. The use of ether as a mutual solvent should be investigated. Since ether has low surface tension, the drying stress might be reduced.

4. Microwave drying of samples which have reached the tertiary drying stage should be investigated as a way of reducing drying times.

5. Since the use of acrysol resins as cross-linking agents appears to have beneficial affects, work in this area should continue, with further variation of reaction parameters.

6. To prevent cracking and fragmentation during drying, the addition of surfactant[11] to the initial preparation could be investigated. Surfactants reduce the interfacial energies which generally cause fragmentation of gels.

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TABLE 1

**Relevant physical properties of solvents and cross-linking reagents used.**

| Reagents/ Solvents | Mol. Wt[10] | Density[10] g/ml | Melting pt. C | Boiling pt. C | Surface[9] Tension at 20 C (dynes/cm) |
|---|---|---|---|---|---|
| t-Butanol $(CH_3)_3COH$ | 74.12 | 0.786 | 25-25.5 | 83 | 20.7 |
| Phenol $C_6H_5OH$ | 94.11 | 1.071 | 40.5-41.5 | 182 | |
| Pinacol $(CH_3)_2 \cdot C(OH) \cdot C(OH) \cdot (CH_3)_2$ | 118.18 | | 40-43 | 171-172 at 739 torr | |
| 1,3 Butanediol $CH_3CH(OH)CH_2OH$ | 90.12 | 1.005 | | 203-204 | |
| 1,4 Butanediol $HO(CH_2)_4OH$ | 90.12 | 1.017 | 16 | 230 | |
| 2,3 Butanediol $CH_3CH(OH)CH(OH)CH_3$ | 90.12 | 0.995 | 25 | 183-184 | |
| Ether $(C_2H_5)_2O$ | 74.12 | 0.706 | | 34.6 | 17 |
| Methanol | 32.04 | 0.791 | -98 | 64.6 | 22 |
| Ethanol | 46.07 | 0.785 | -130 | 78 | 23 |
| Tetraethyl Orthosilcate (TEOS) $Si(OC_3)_4$ | 208.33 | 0.934 | | 168 | |
| Silicon (IV) Chloride $SiCl_4$ | 169.60 | 1.340 | -70 | 57.6 | |
| Water | 18 | 1 | 0 | 100 | 73 |
| Formamide $HCONH_2$ | 45.04 | | | | 58 |

TABLE 2

Physical properties of dry aerogel samples.

| Sample # | Density ($g/cm^3$) | Thickness (cm) | Porosity | % Transmittance at 400 nm | % Transmittance at 800 nm |
|---|---|---|---|---|---|
| 870623/K-C.2 | 0.63 | 0.35 | 0.71 | 8 | 40 |
| 870626/K-A.2 | 0.48 | 0.25 | 0.78 | 7 | 34 |
| 870702/K-B.2 | 0.65 | 0.22 | 0.70 | 11 | 40 |
| 870703/K-A.2 | 0.59 | 0.30 | 0.73 | 4 | 52 |
| 870703/K-A.3 | 0.59 | 0.30 | 0.73 | 3 | 40 |
| 870703/K-C.3 | 0.59 | 0.30 | 0.73 | 1 | 56 |
| 870806/K-A.2 | 0.68 | 0.28 | 0.69 | 13 | 70 |
| 870707/K-B.3 | 0.55 | 0.40 | 0.75 | 26 | 47 |
| 870717/K-A.2 | 0.87 | 0.24 | 0.60 | 9 | 47 |
| 870717/K-A.1 | 0.69 | 0.22 | 0.69 | 10 | 45 |
| 870722/K-B | 0.63 | 0.32 | 0.71 | 8 | 52 |
| 870723/K-C.1 | 0.63 | 0.33 | 0.71 | 7 | 42 |
| 870723/K-C.3 | 0.60 | 0.27 | 0.73 | 7 | 57 |
| 870723/K-D.1 | 0.50 | 0.30 | 0.77 | 18 | 43 |
| 870723/K-D.3 | 0.49 | 0.34 | 0.78 | 3 | 30 |
| 870723/K-E | 0.71 | 0.32 | | 15 | 48 |
| 870806 | 0.67 | 0.30 | 0.70 | 5 | 21 |
| 870810 | 0.57 | 0.39 | 0.74 | 3 | 40 |
| 870812 | 0.37 | 0.47 | 0.83 | 0 | 28 |
| 870814/1 | 0.50 | 0.35 | 0.77 | 9 | 23 |
| 870820 | 0.62 | 0.44 | 0.72 | 23 | 42 |
| 870821 | 0.53 | 0.46 | 0.76 | 4 | 35 |
| 880120 | 1.84 | 0.17 | 0.16 | 67 | 70 |
| 871214/2 | 0.92 | 0.25 | 0.58 | 33 | 60 |
| 871109D | 0.79 | .51 | 0.64 | | |

TABLE 3

MIXING VOLUMES OF REAGENTS IN THE PREPARATION OF VARIOUS GELS

| Sample # | VOLUME OF REAGENTS MIXED (ml) | | | | | | | | | | | | | | Solv. ex. | Gel time (hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Me | tb | Ph | Pin | Er | Te | Tm | Fm | 1,4bd | 1,3bd | Water | Other | HCl (aq) | $NH_4F$, $NH_4OH$, HFl | | |
| 870623/K-C.2 | 29 | | | | | 12 | | 17 | | | | | 6 (ph=6) | | tb | ~144 |
| 87026/K-A.2(D) | 6.3 | | | | | 8.5 | | 6.3 | 6.3 | | 2.0 | | 4 (ph=3) | | tb | ~72 |
| 870703/K-A.2 | 10 | | | | | 12.8 | | 10 | 9.5 | | 3.0 | | 6 (ph=6) | | tb | ~144 |
| 870706/K-A.2 | 10 | | | | | 12.8 | | 10 | | 9.5 | 3.0 | | 6 (ph=6) | | Pin | ~168 |
| 870717/K-A.2 | 29 | | | | | 12 | | 17 | | | | | 5 (ph=6) | | tb | ~240 |
| 870722/K-B | 73 | | | | | 25.4 | | 57 | | | 5 | | 8 (ph=6) | | tb | ~240 |
| 870723/K-B | 36 | | | | | 12 | | 18 | | | | | 6 (ph=6) | | tb | ~192 |
| 870723/K-C | 30 | | | | | 13 | | 10 | 10 | | 3 | | 6 (ph=6) | | tb | ~144 |
| 87023/K-D | 31 | | | | | 13 | | 19 | 7 | | 2.5 | | 4 (ph=6) | | tb | ~144 |

tb = tertiary butanol

TABLE 3 (Cont'd)

MIXING VOLUMES OF REAGENTS IN THE PREPARATION OF VARIOUS GELS

| Sample # | VOLUME OF REAGENTS MIXED (ml) | | | | | | | | | | | | | | Solv. ex. | Gel time (hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Me | tb | Ph | Pin | Er | Te | Tm | Fm | 1,4bd | 1,3bd | Water | Other | HCl(aq) | $NH_4F$, $NH_4OH$, HFl | | |
| 870723/K-E | 31 | | | | | 13 | | 19 | | | 2.5 | 7 (2,3bd) | 4 (ph=6) | | tb | ~168 |
| 870806 | | 36 | | | | 12 | | 18 | | | | | 6 (ph=6) | | tb | ~264 |
| 870810 | | 30 | | | | 12.8 | | 18 | 10 | | | | 6 (ph=6) | | tb | ~364 |
| 870812 | | | 22gm (molten) | | | 13 | | 18 | 15 | | | | 6 (ph=6) | | Ph | ~1 |
| 870814/1 | 38 | | | | | 19 | | 25 | | | | | | 6 (ph=8) | tb | ~72 |
| 870814/2 | 43 | | | | | 17 | | 25 | 15 | | | | | 7 (ph=8) | tb | ~72 |
| 870820 | 30 | | | | | 14 | | 19 | | | | 9 (2,3bd) | | 6 (ph=10) | tb | 2 |
| 870821 | 35 | | | | | 17 | | 23 | | | | 10 (2,3bd) | 6 (ph=6) | | tb | ~168 |
| 870918/1 | 80 | | | | | 26 | | 60 | | | 5 | | 8 (ph=6) | | tb | ~264 |

TABLE 3 (Cont'd)

MIXING VOLUMES OF REAGENTS IN THE PREPARATION OF VARIOUS GELS

| Sample # | VOLUME OF REAGENTS MIXED (ml) | | | | | | | | | | | | | | Solv. ex. | Gel time (hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Me | tb | Ph | Pin | Er | Te | Tm | Fm | 1,4bd | 1,3bd | Water | Other | HCl(aq) | $NH_4F$, $NH_4OH$, HFl | | |
| 870918/ | 35 | | | | | 13 | | 19 | | 9 | 3 | | 4(ph=6) | | tb | ~264 |
| 871001/2 | 23 | | | | | 20 | | 10 | | 5 | | | 7(ph=6) | | tb | 360 |
| 871112/1 | | | | 58gm (molten) | | 26 | | 23 | | 24 | | | 14(ph=6) | | Pin | ~240 |
| 871204/1 | 25 | | | | | 9 | | 8 | | 8 | 5 | 0.8 (Glycerol) | | 2(ph=10) | tb | ~0.17 |
| 871214/2 | 20 | | | | | 9 | | 9 | | 7 | 7 | 0.5 (Glycerol) | 0.5(ph=10) | | tb | ~48 |
| 871214/3 V | 32 | | | | | 10 | | 10 | | | 8 | 0.5 (Glycerol) | | 0.5 (ph=10) | tb | ~168 |
| 871228 | 20 | | | | | 7 | | 13 | | | 3.5 | 0.6 (Glycerol) | | 0.5 (ph=10) | tb | ~72 |
| 880107/1 | 32 | | | | | 10 | | 12 | | 10 | 8 | | | 0.6 (ph=10) | tb | 24 |
| 880107/3 | 25 | | | | | 16 | | 15 | | 15 | 12 | | | 0.7 (ph=10) | tb | 24 |
| 880108/1 | | | 21gm (molten) | | | 15 | | 17 | | 15 | 8 | | | 0.5 (ph=10) | Ph | 72 |

V=vaseline coated mold

TABLE 3 (Cont'd)

MIXING VOLUMES OF REAGENTS IN THE PREPARATION OF VARIOUS GELS

| Sample # | VOLUME OF REAGENTS MIXED (ml) | | | | | | | | | | | | | | Solv. ex. | Gel time (hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Me | tb | Ph | Pin | Er | Te | Tm | Fm | 1,4bd | 1,3bd | Water | Other | HCl(aq) | $NH_4F$, $NH_4OH$, HFl | | |
| 880115 | 25 | | | | | 16 | | 12 | | 10 | 8 | | | 0.3 (ph=10) | tb | 24 |
| 880129 | 20 | | | | | 8 | | 10 | | 10 | 2.6 | | | 0.4 (ph=10) | Pin | 48 |
| 880203/1 V | 21 | | | | | | 20 | 10 | | 10 | 10 | | | | tb | 18 |
| 880210 ⊗ | 80 | | | | | | 40 | 15 | | 15 | 20 | | | | tb | 18 |
| 880212/1 V | 25 | | | | | | 20 | 10 | | | 5 | 10 (Acrysol WS-24) | | | | 1 |
| 880212/2 | 25 | | | | | | 20 | | | | 5 | 10 (Acrysol WS-24) | | | | 2 |
| 880217 | 30 | | | | | 17 | | 10 | | 10 | 5 | | | 0.8 (ph=8) | tb/Pin | ~168 |
| 880219 | 30 | | | | | 15 | | 10 | | 10 | 5 | | | 1 | /Pin | ~144 |
| 880301 V⊗ | 100 | | | | | 45 | | 10 | | | | 17 (Acrysol WS-32 1:50aq) | | 1 (ph=8) | Pin | 18 |

V= vaseline coated mold
⊗ = 15cm dia mold

TABLE 3 (Cont'd)

MIXING VOLUMES OF REAGENTS IN THE PREPARATION OF VARIOUS GELS

| Sample # | VOLUME OF REAGENTS MIXED (ml) | | | | | | | | | | | | | | Solv. ex. | Gel time (hr) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Me | tb | Ph | Pin | Er | Te | Tm | Fm | 1,4bd | 1,3bd | Water | Other | HCl(aq) | $NH_4F$, $NH_4OH$, HFl | | |
| 880303/1[V] | | | | | | 23 | | 10 | | | | (Acrysol WS-50 1:25 in Mc) | 1.3 (ph=6) | | | 24 |
| 880304 [V] A,B | 70 | | | | | 30 | | 12 | | | | 10 (Acrysol WS-32 1:50 aq) | | 1.3 (ph=8) | Pin | 18 |
| 880309 [V⊗] | 90 | | | | | 40 | | 15 | | | 13 | 5 (Acrysol WS-50) | | 2 (ph=8) | Pin | 18 |
| 880310/1[V⊗] | 100 | | | | | 40 | | 17 | | | | 14 (Acrysol WS-50 1:50 aq) | | 2 (ph=8) | Pin | 18 |
| 880310/2[V⊗] | 80 | | | | | 40 | | 22 | | | | 13 (Acrysol WS-50 1:50 aq) | | 2 (ph=8) | Pin | 18 |
| 880319 | 20 | | | | 20 | | 20 | 5 | | 5 | 5.8 | | | 1.5 (ph=8) | Er | 18 |
| 880408[V] | 20 | | | | 20 | | 20 | 5 | | 5 | 5.8 | | | 1.5 (ph=8) | Er | 18 |
| 880120 | | | | | | | 20 | | | | 5 | | | | | |
| | | | | | | | | | | | | | | | | |

15 cm dia mold

V= vaseline coated mold

TABLE 4

OBSERVATIONS ON DRYING OF ALCOGEL SAMPLES

| SAMPLE # | DRYING CONDITIONS | OBSERVATIONS | | | | | |
|---|---|---|---|---|---|---|---|
| | | Drying time | Transparency | Warping | Fragmentation | Shrinkage | General |
| 870623/K-C.2 | FH,CP | ~16Weeks | Translucent | No | Yes | >50% | Broke into many pieces, several internal cracks. |
| 870626/K-A.2(D) | FH,CP | ~16 " | " | " | No | > 50% | No internal cracks. |
| 870703/K-A.2 | FH,CP | ~15 " | " | " | " | > 50% | " " " |
| 870706/K-A.2 | FH,CP | ~16 " | " | " | Yes | >50% | Broke to many pieces |
| 870717/K-A.2 | FH,CP | ~16 " | " | " | " | >50% | Many small pieces, no internal cracks, withstood pyrolysis at 500°C |
| 870722/K-B | FH,CP | ~16 " | " | " | " | >50% | " |
| 870723/K-B | FH,CP | ~16 " | " | " | " | > 50% | " |
| 870723/K-C.1 | FH uP | ~16 " | " | " | " | >50% | Many pieces, but they survived pyrolysis at 500°C without new cracks appearing. |
| 870723/K-C.3 | DSR,RT,VM,uP | ~18 " | " | " | " | > 50% | Many translucent pieces, one 2cm² piece became almost transparent after pyrolysis at 500°C. |
| 870723/K-D.3 | " " | ~ 20 " | " | " | " | > 50% | Many small pieces, no internal cracks. |

FH = fumehood, CP = covered plate, DSR = Desiccator, RT = Room temperature

VM = Vacuum, uP = uncovered plate

TABLE 4 (Cont'd)

OBSERVATIONS ON DRYING OF ALCOGEL SAMPLES

| SAMPLE # | DRYING CONDITIONS | OBSERVATIONS | | | | | |
|---|---|---|---|---|---|---|---|
| | | Drying time | Transparency | Warping | Fragmentation | Shrinkage | General |
| 870723/K-E | FH,CP | ~18Weeks | Translucent | No | Yes | >50% | No cracks, survived pyrolysis at 500°C, transmission improved by 15-20% after pyrolysis. |
| 870806 | FH,CP | ~15 " | " | " | " | >50% | Many pieces but strong, survived pyrolysis at 500°C. No internal cracks. |
| 87010 | FH,CP | ~12 " | " | " | " | >50% | Yellowish pieces, no internal cracks, strong. |
| 870812 | FH,CP | ~ 14 " | " | " | " | >50% | Many pieces, strong survived pyrolysis at 500°C without new cracks developing. |
| 870814/1 | FH,CP | ~14 " | " | " | " | >50% | Many small pieces survived pyrolysis at 500°C without new cracks developing. |
| 870814/2 | FH,CP | ~14 " | " | " | " | >50% | Many small pieces, no internal cracks. |
| 870820 | FH,CP | ~14 " | " | " | No | >50% | 5 small pieces survived pyrolysis at 500°C, almost transparent. |
| 870821 | FH,CP | ~14 " | " | " | " | >50% | Many small pieces, survived pyrolysis at 500°C without any new cracks. |

TABLE 4 (Cont'd)

OBSERVATIONS ON DRYING OF ALCOGEL SAMPLES

| SAMPLE # | DRYING CONDITIONS | OBSERVATIONS | | | | | |
|---|---|---|---|---|---|---|---|
| | | Drying time | Transparency | Warping | Fragmentation | Shrinkage | General |
| 870918/1 | FH,CP | ~ 12Weeks | Translucent | No | Yes | >60% | Broke into many pieces,however survived pyrolysis at 500°C. |
| 870918/2 | FH,CP | - | " | " | " | >50% | Broke into five pieces, at the tertiary drying phase. |
| 871001/2 | FH,CP | ~10 " | " | " | " | " | The pieces do not have any cracks, survived pyrolysis at 500°C. |
| 871112/1 | FH,CP | - | " | " | " | ~40% | Broke into two pieces, in the secondary drying stage. |
| 871204/1 | FH,CP | - | " | " | " | " | Three cracks, three pieces, secondary-tertiary drying phase. |
| 871214/3 | FH,CP | - | Opaque | " | " | ~50% | Broke into more than 8 pieces, in the tertiary drying stage. |
| 871228 | FH,CP | - | Translucent | " | " | ~40% | Broke into 6 pieces, the largest one~3cm² in area, in the tertiary drying stage. |
| 880107/1 | FH,CP | - | Transparent | " | No | " | Monolithic gel, in the secondary - tertiary drying stage. |
| 880107/3 | FH,CP | - | " | " | " | ~50% | " " |
| 880108/1 | FH,CP | - | Translucent | " | " | ~15% | Monolithic gel, in the secondary stage of drying. |

TABLE 4 (Cont'd)

OBSERVATIONS ON DRYING OF ALCOGEL SAMPLES

| SAMPLE # | DRYING CONDITIONS | OBSERVATIONS | | | | | |
|---|---|---|---|---|---|---|---|
| | | Drying time | Transparency | Warping | Fragmentation | Shrinkage | General |
| 880115 | FH,CP | - | Transparent | No | Yes | ~10% | Monolithic gel, in the primary-secondary drying stage. |
| 880129 | FH,CP | - | " | " | No | ~15% | No cracks, in the secondary drying stage. |
| 880203/1 | FH,CP | - | Translucent | " | Yes | ~50% | 4 pieces, one as large as 3cm², small cracks, in the secondary-tertiary drying stage. |
| 880210 | FH,CP | - | Transparent | " | " | ~20% | 5 pieces, in the secondary drying stage. |
| 880212/1 | FH,CP | - | Opaque | " | " | ~30% | Many cracks, in the tertiary drying stage. |
| 880212/2 | FH,CP | - | " | " | " | " | Broke into two halves with many cracks, in the tertiary drying stage. |
| 880217 | FH,CP | - | Transparent | " | No | ~10% | In the secondary drying stage. |
| 880219 | FH,CP | - | " | " | " | " | " " |
| 88301 | FH,FCA,CP | - | Translucent | " | " | ~25% | In the secondary drying stage. |
| 88303/1 | " " | - | " | " | " | ~10% | " " |

FCA = flowing atmosphere of compressed air

TABLE 4 (Cont'd)

OBSERVATIONS ON DRYING OF ALCOGEL SAMPLES

| SAMPLE # | DRYING CONDITIONS | OBSERVATIONS | | | | | |
|---|---|---|---|---|---|---|---|
| | | Drying time | Transparency | Warping | Fragmentation | Shrinkage | General |
| 88304 | FH,CP | - | Transparent | No | Yes | ~ 30% | Cracks in the periphery, secondary drying stage. |
| 88304-B | " " | - | " | " | No | ~ 25% | In the secondary drying stage. |
| 88309 | FH,FCA,CP | - | Translucent | " | " | ~ 30% | In the secondary drying stage. |
| 880310/1 | FH,FCA,CP | - | " | " | " | 20% | " " |
| 880310/2 | " " | - | " | " | " | 20% | " " |
| 880319 | FH,CP | - | Transparent | " | " | 40% | In the tertiary drying stage. |
| 880408 | " " | — | " | " | " | 5% | In the primary drying stage. |
| 880120 | " " | 8Weeks | " | " | Slight | 30% | Some cracks developed but the largest piece (12cm$^2$) survived pyrolysis at 500°C; the piece was glass-like. |

# APPENDIX I

Fig 1A

4/13/88

WAVELENGTH SCAN REPORT

Aerogel
870723/k-E
~ 4.2 mm thick
before pyrolysis

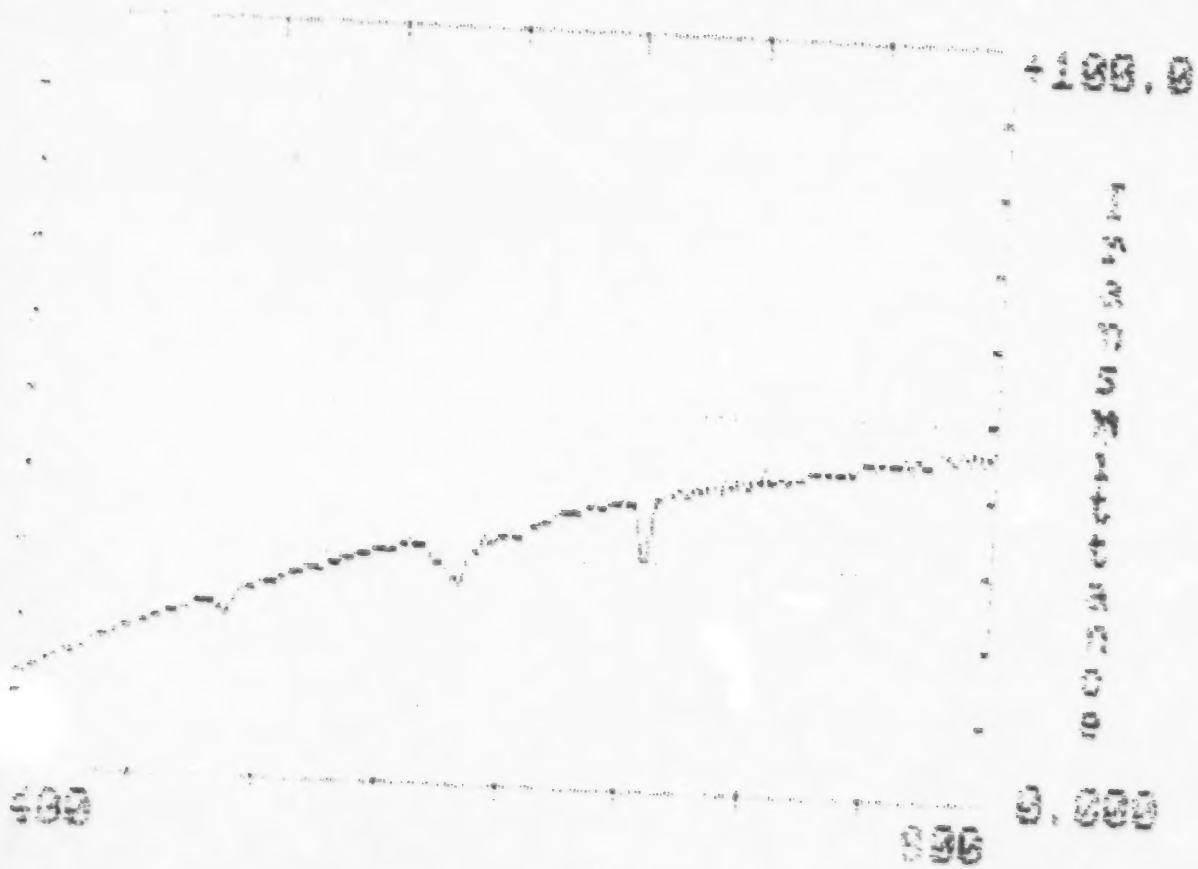

Fig 1B

4/14/88

PCG

Aerogel 870723/k-E
Pyrolyzed at 550c

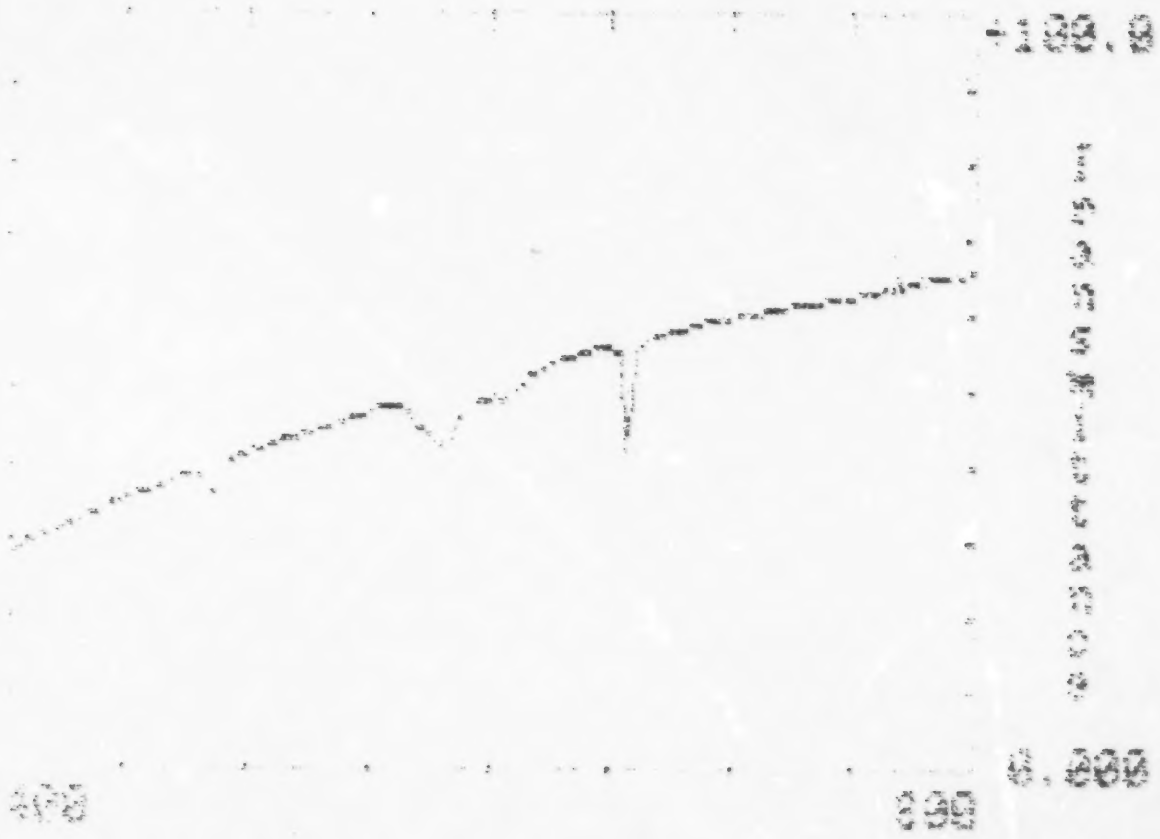

Fig 2A

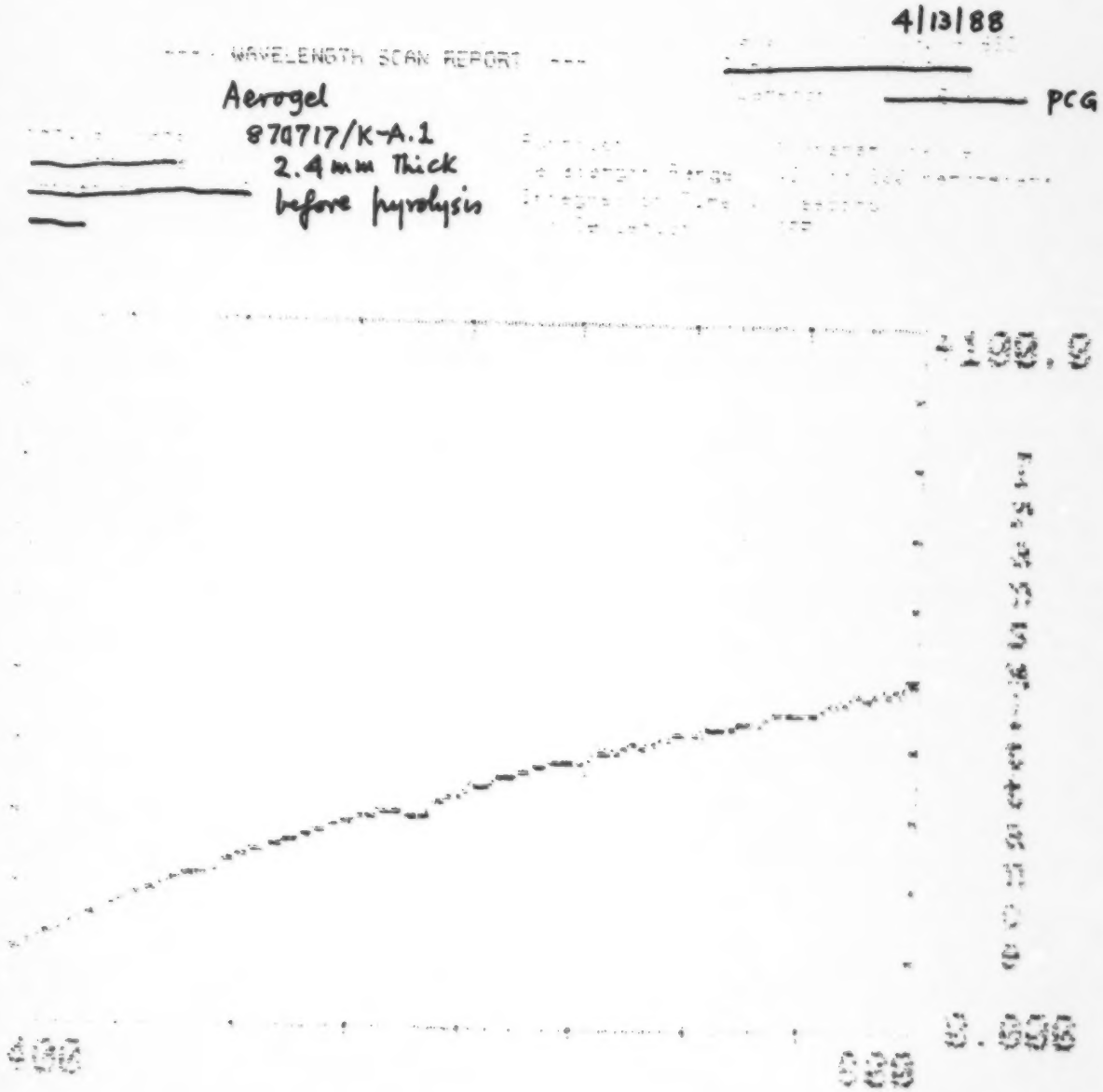
4/13/88
--- WAVELENGTH SCAN REPORT ---
PCG
Aerogel
870717/K-A.1
2.4 mm Thick
before pyrolysis
100.0
0.00
400
800

Fig 2 B

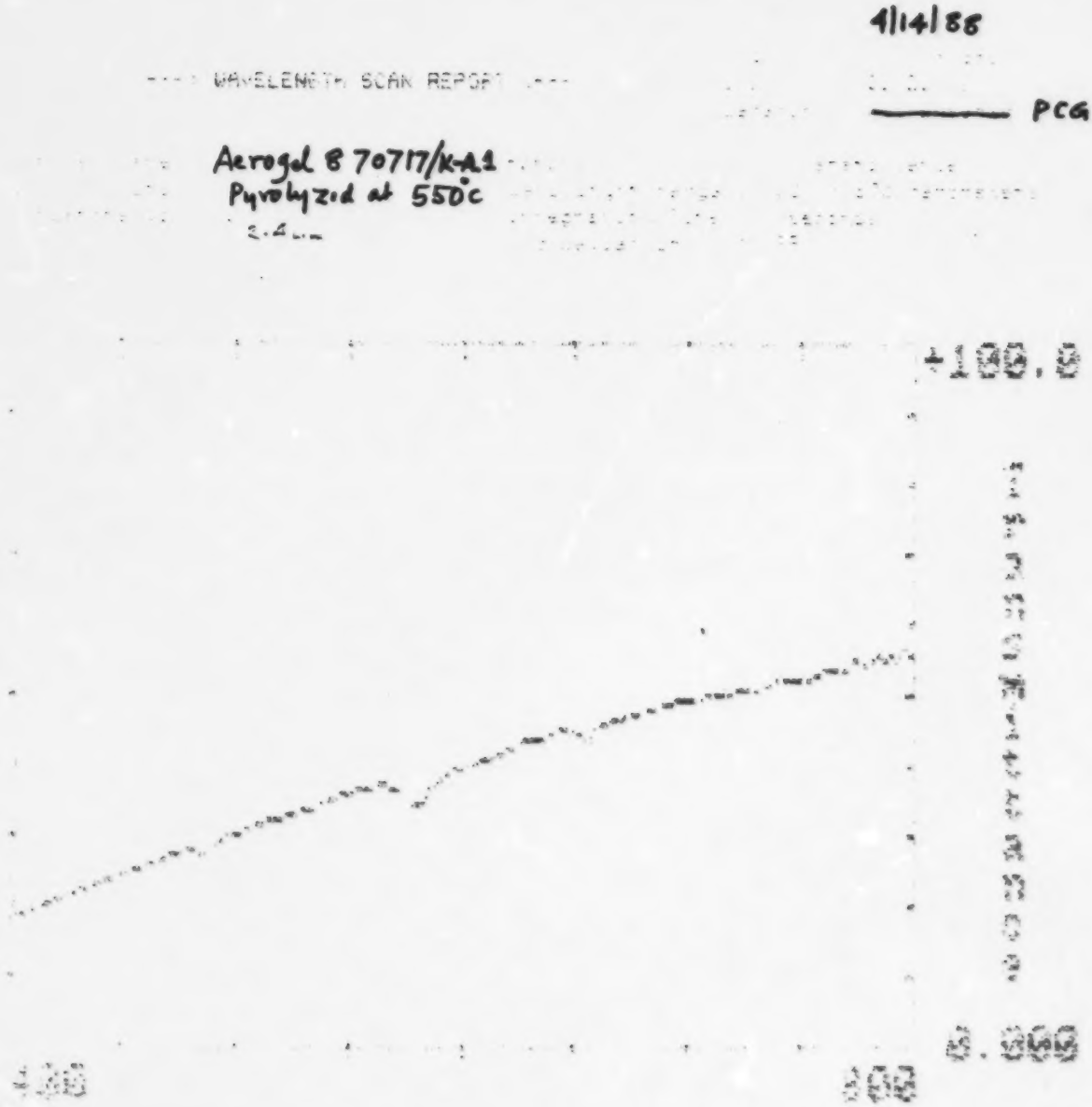
4/14/88
WAVELENGTH SCAN REPORT
PCG
Aerogel B 70717/K-A1
Pyrolyzed at 550C
2.4
+100.0
0.000
400
300

Fig 3A

4/13/88

WAVELENGTH SCAN REPORT

PEG

Aerogel
870706/K-A.2
2.5 mm against air
before pyrolysis

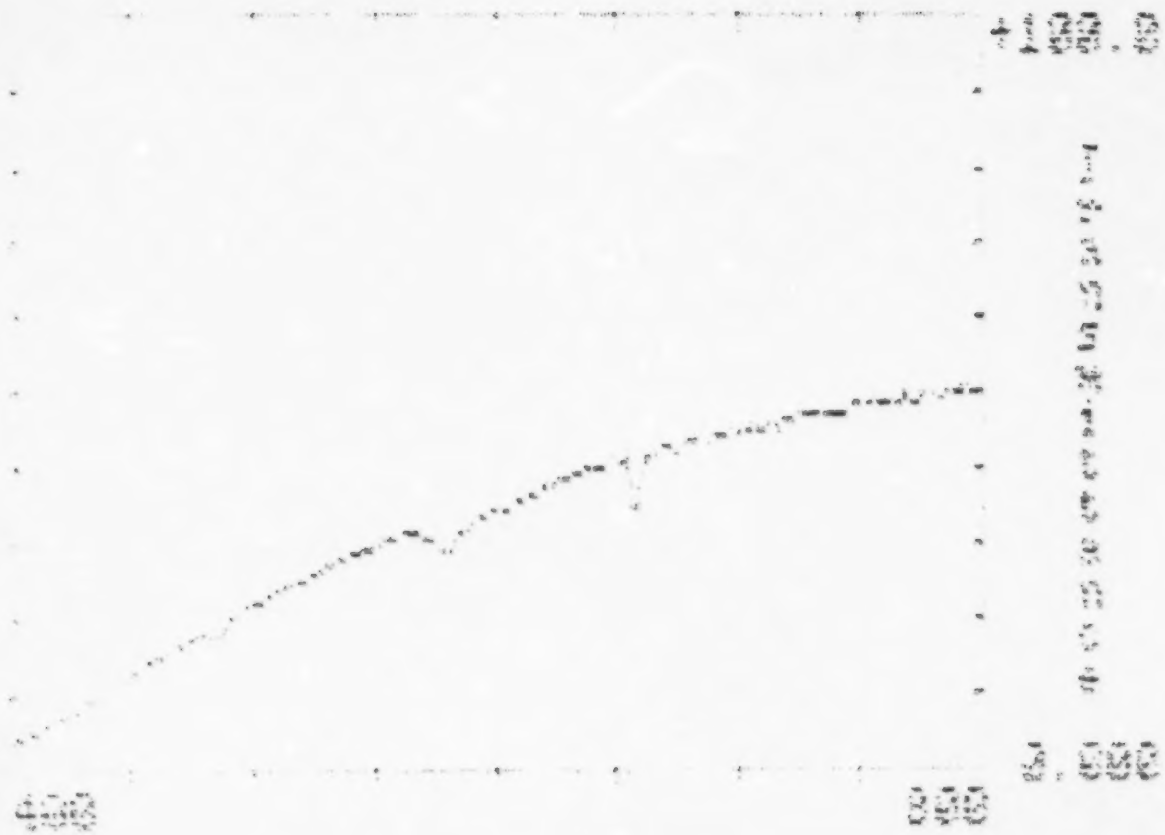

Fig 3B

4/14/88

--- WAVELENGTH SCAN REPORT ---

PCG

Aerogel 870706/8-A.2
hydrolyzed at 550c

2.5 mm

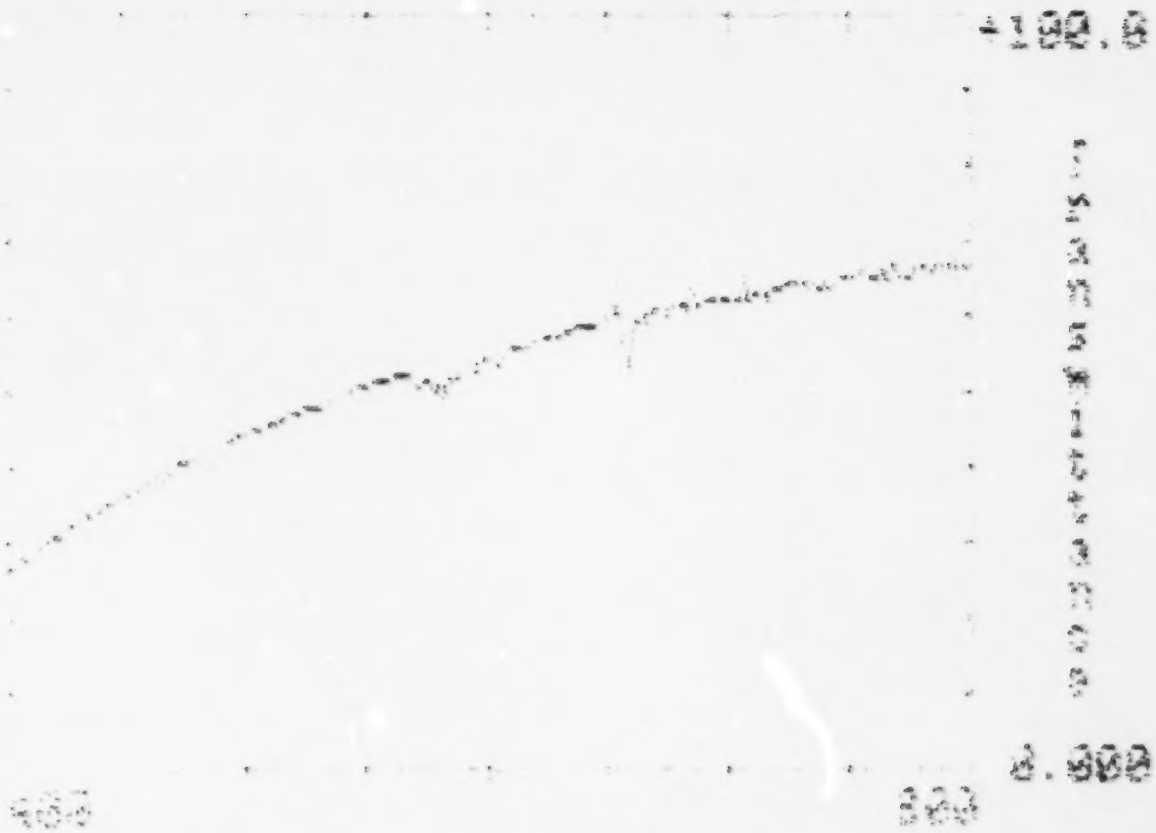

Fig 4A

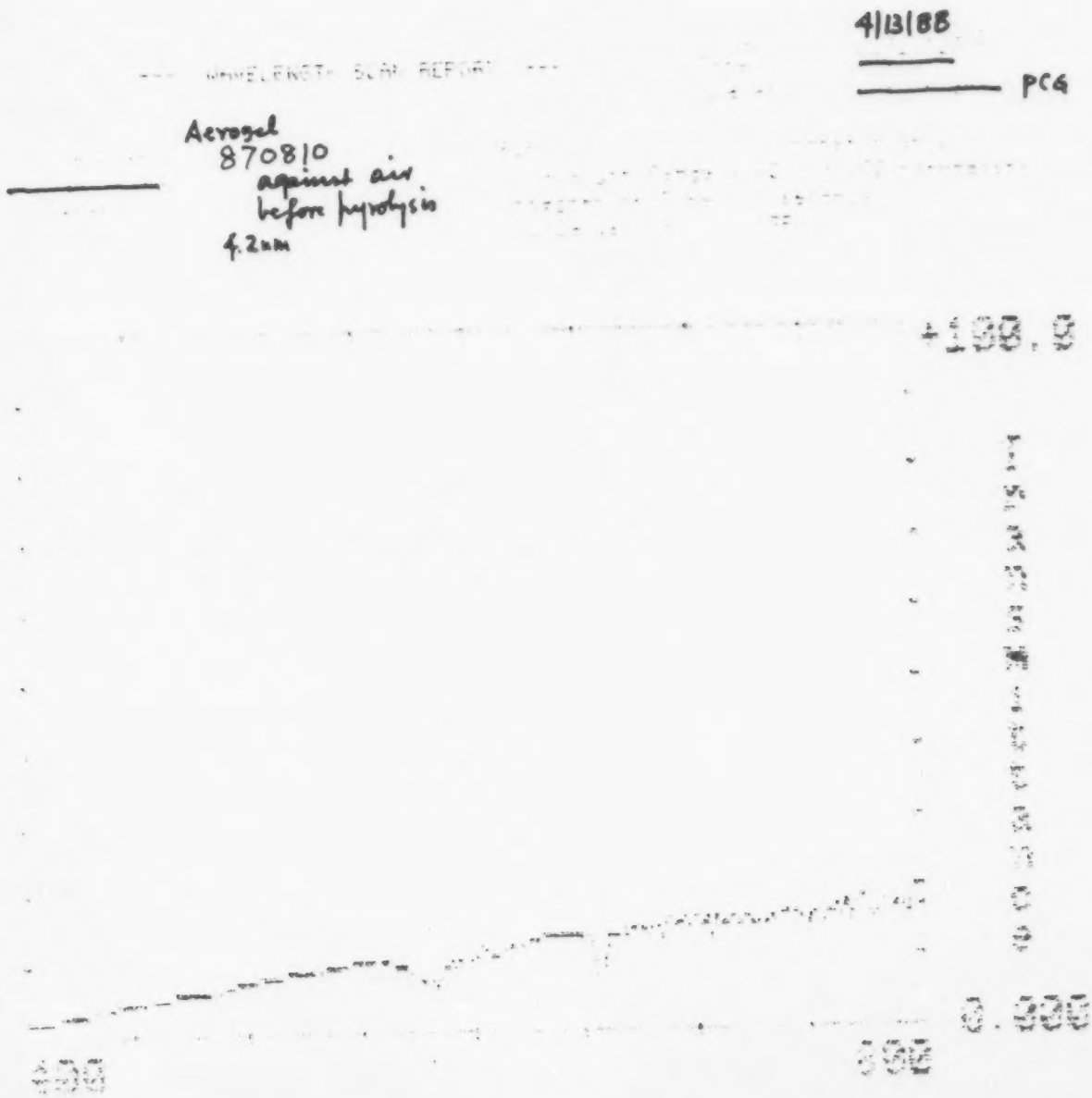
4/13/88
PC4
Aerogel
870810
against air
before hydrolysis
4.2nm
+100.0
0.000
400
300

Fig 4B

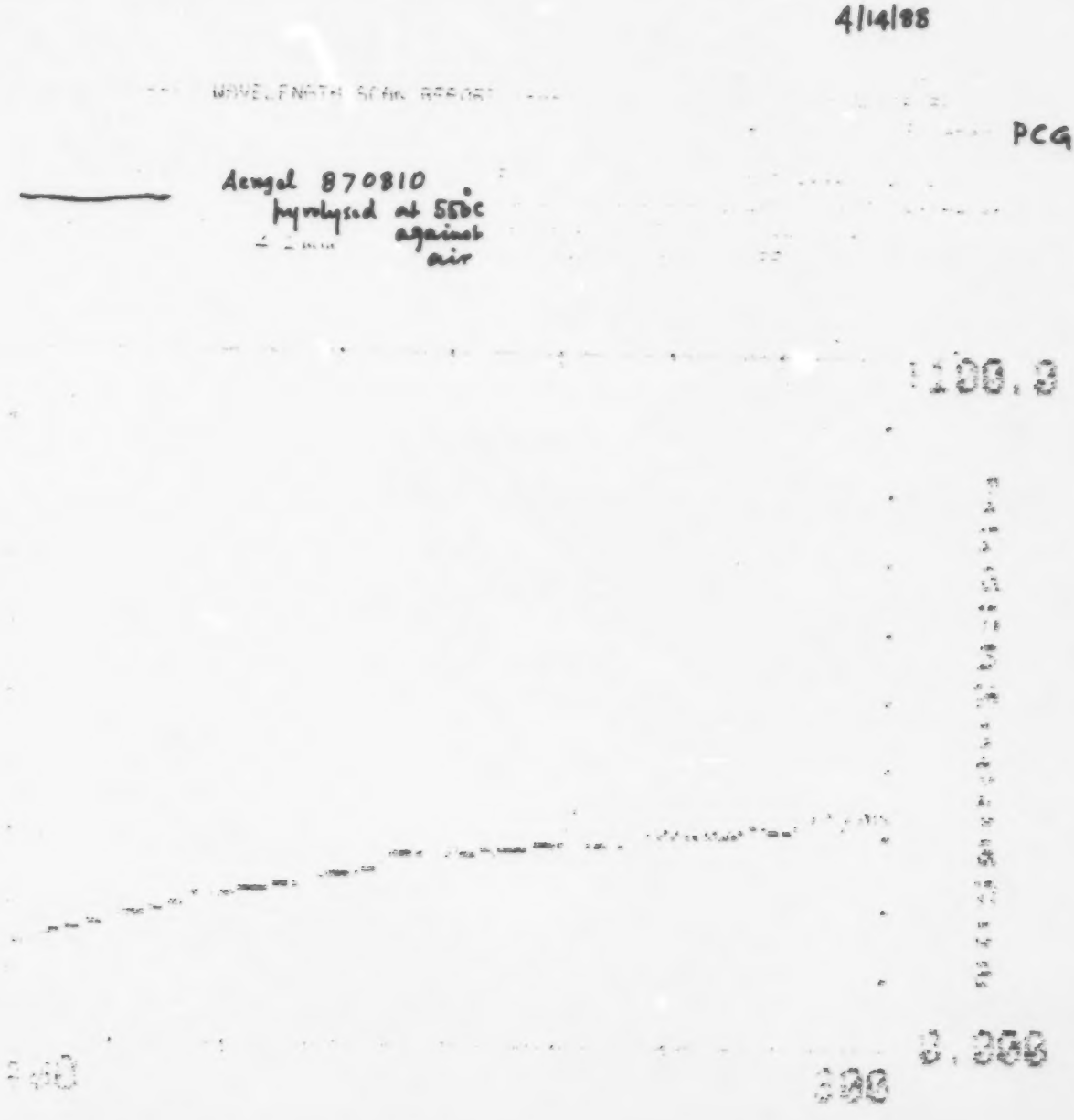
4/14/88
PCG
Aerogel 870810
hydrolysed at 55°C
against
air
1200.0
3.200
200
200

Fig 5

---> WAVELENGTH SCAN REPORT <---

Date : 10-27-1987
Time : 15:01:46
Operator : Not Entered

Sample Name : Silica Aerogel
Solvent Name : Sample No. 870706/K-A.2
Concentration : 0
Units :
Average Thickness 2.8 mm

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

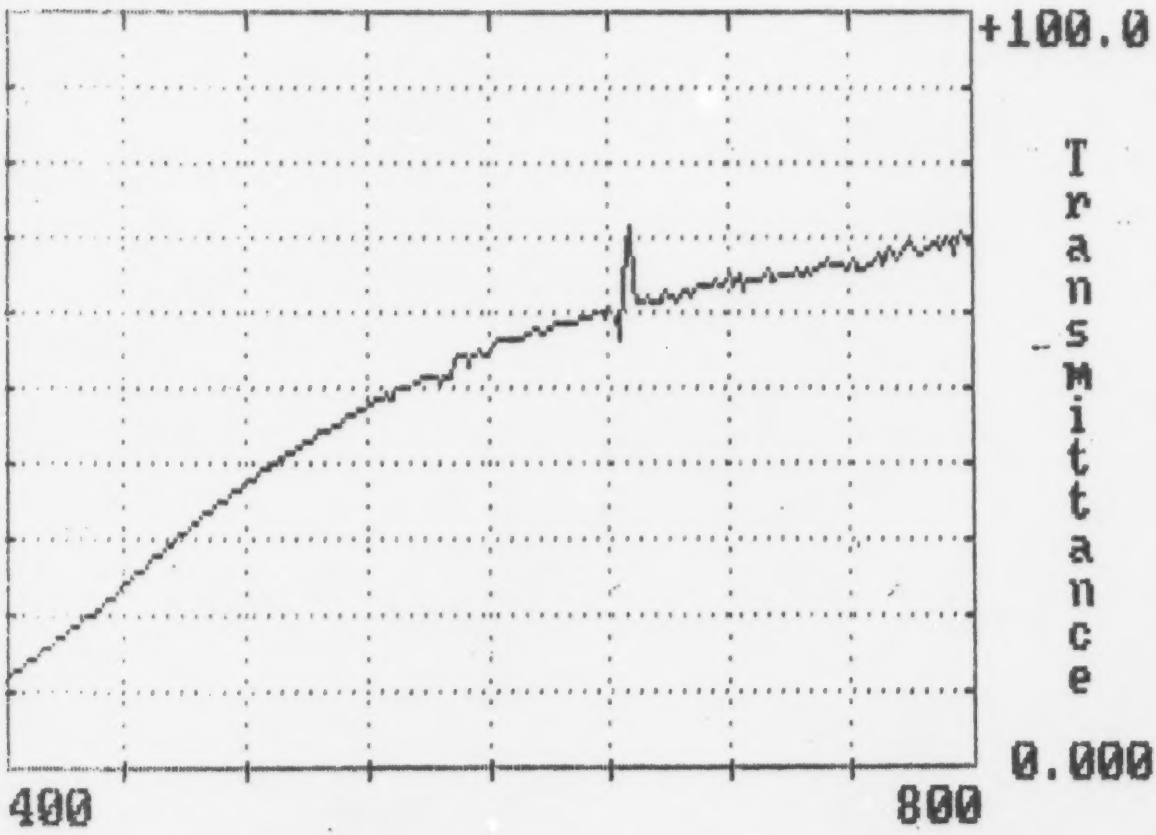

Fig 6

---> WAVELENGTH SCAN REPORT <---

Date 27 11 [illegible]7

SILICA AEROGEL

Sample Name : 870717/K-A.2

Function : % transmittance

Concentration : 0

Integration Time [illegible]

Units

Standard Deviation : OFF

Average Thickness 2.4 mm

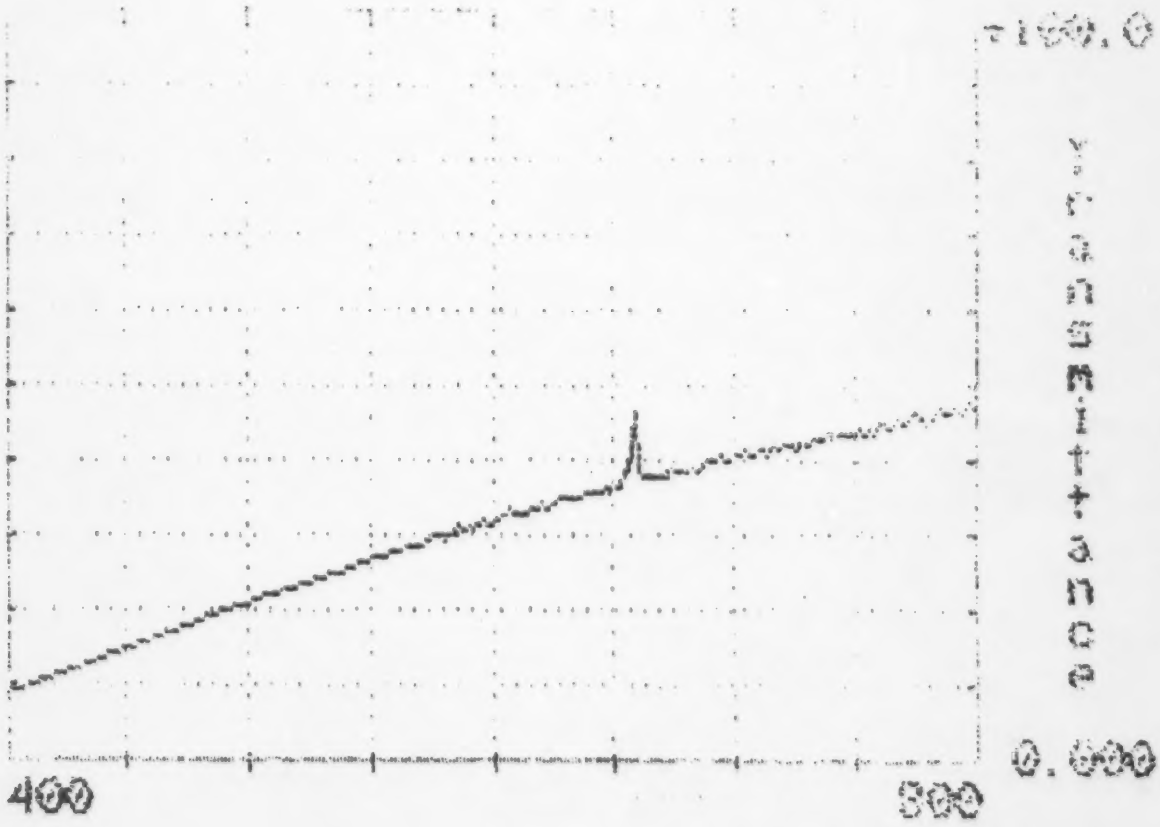

Fig 7

---> WAVELENGTH SCAN REPORT <---

Date : 27-11-87
Time :
Operator : Not Entered

SILICA AEROGEL

Sample Name : 870623/K-C.2
Solvent Name :
Concentration : 0
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

Average Thickness 3.5 mm.

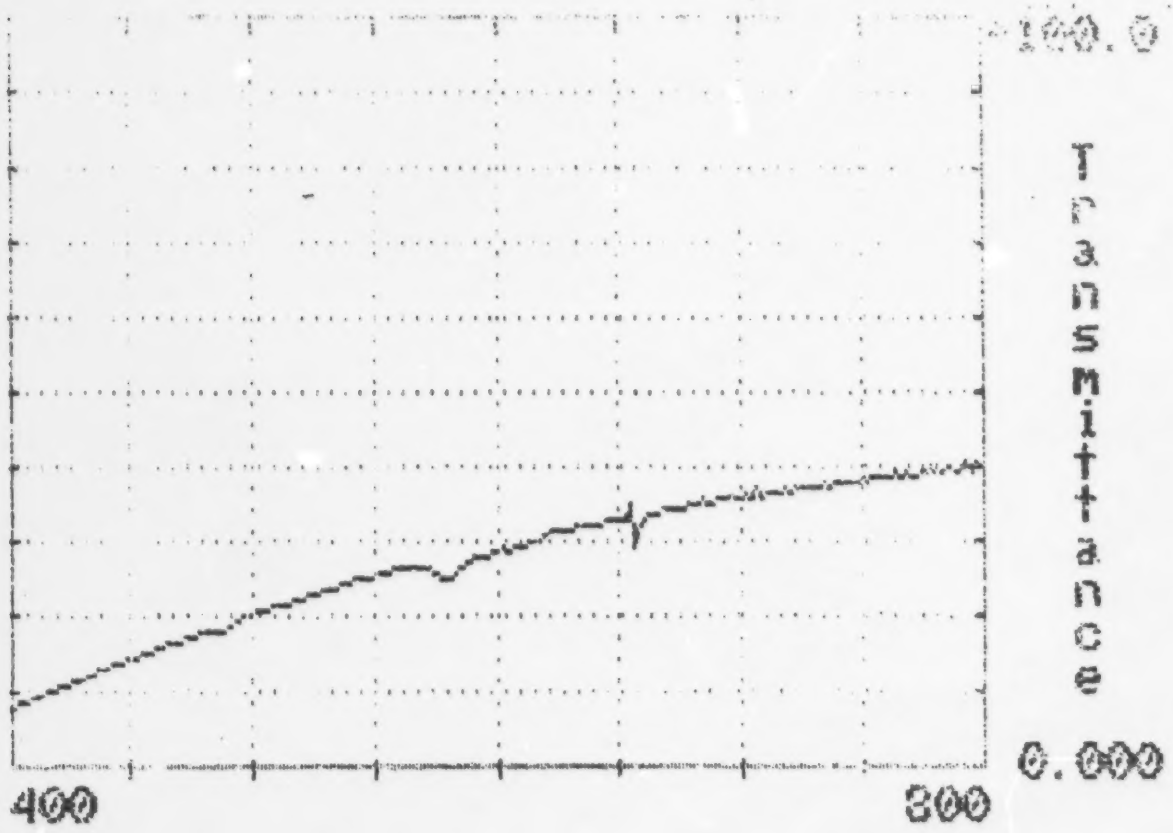

Fig. 8

---> WAVELENGTH SCAN REPORT <---

Aerogel

870810

Sample :
Solve :
Conce : @ Thickness 0.39 cm
Units :

Date :
Time :
Operator :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

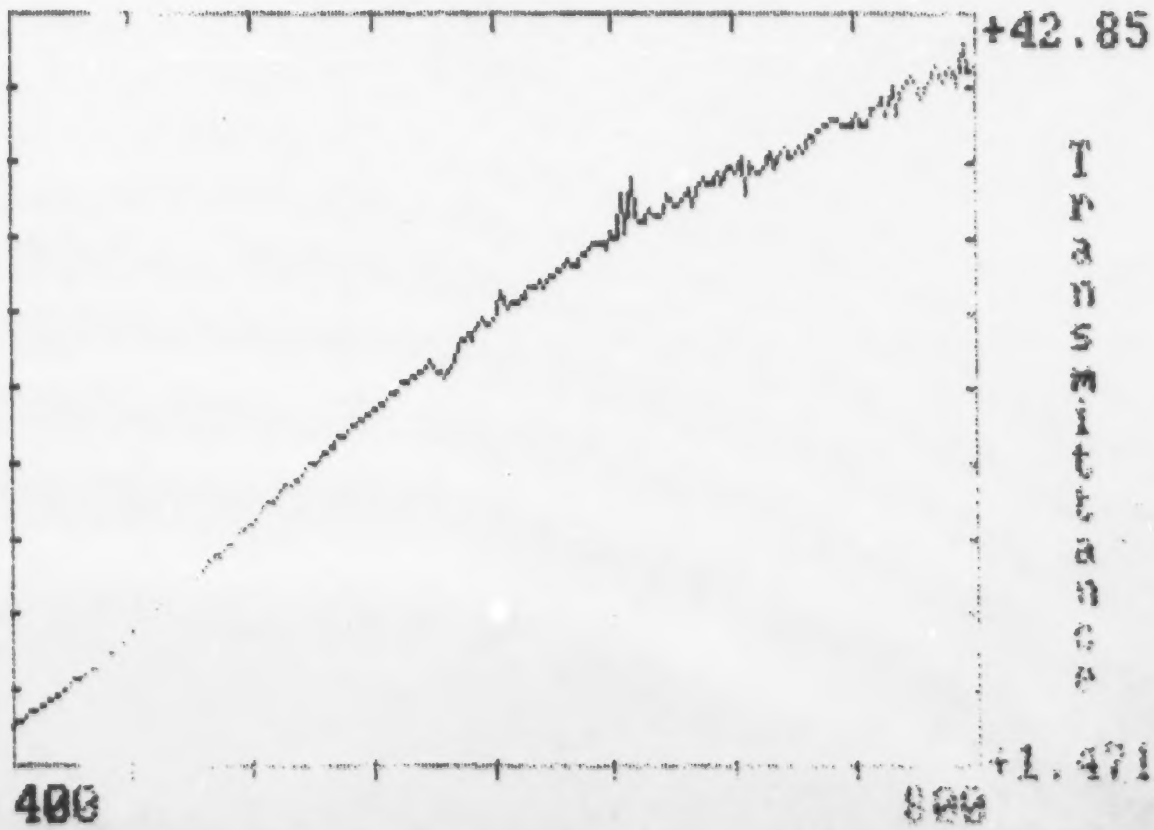

Fig. 9

---> WAVELENGTH SCAN REPORT <---

Aerogel

870717/k-A.1

Sample

Solvent

Concentration Thickness 0.22cm

Units

Function : % Transmittance

Wavelength Range : 400 to 800 nanometers

Integration Time : 1 second

Std Deviation : OFF

Date

Time

Operator

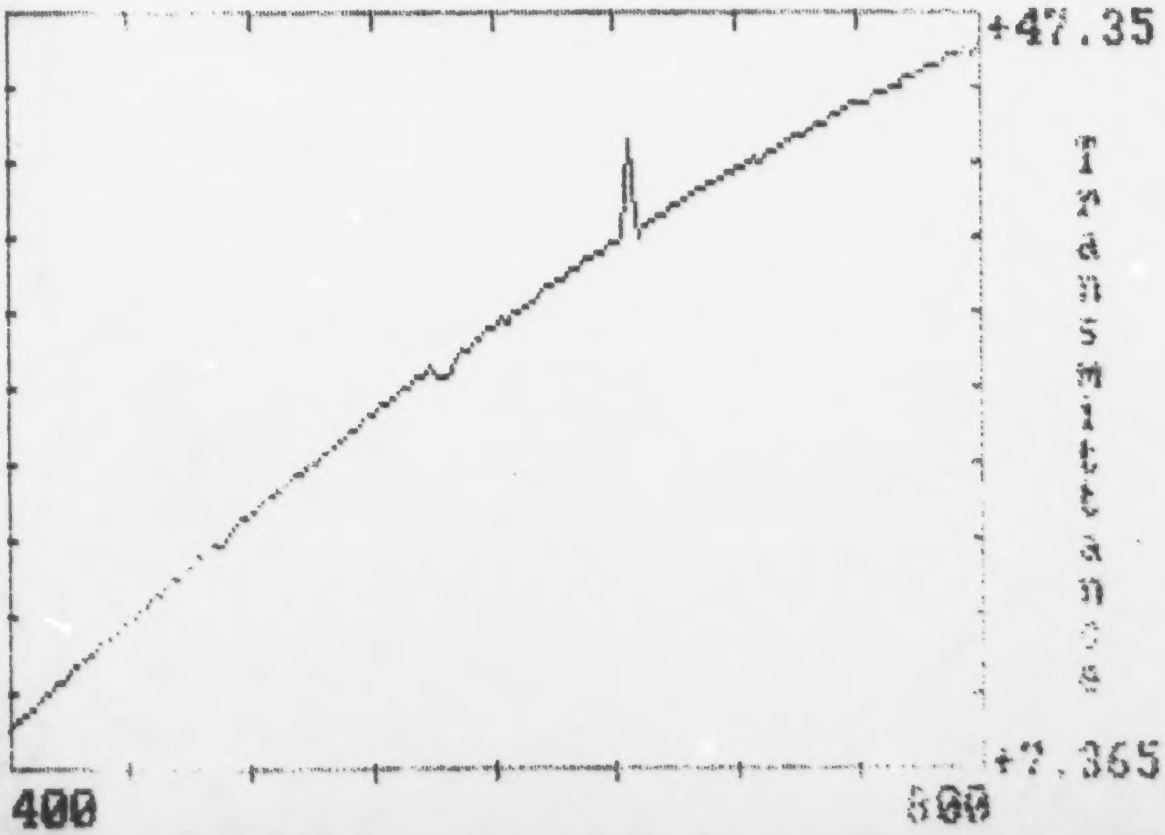

Fig: 10

FIG.

---> WAVELENGTH SCAN REPORT <---

870702/K-B.2
Phenol Exchanged Aerogel

Sample :
Solvent :
Concentration : Thickness 0.22 cm
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 second
Std Deviation : OFF

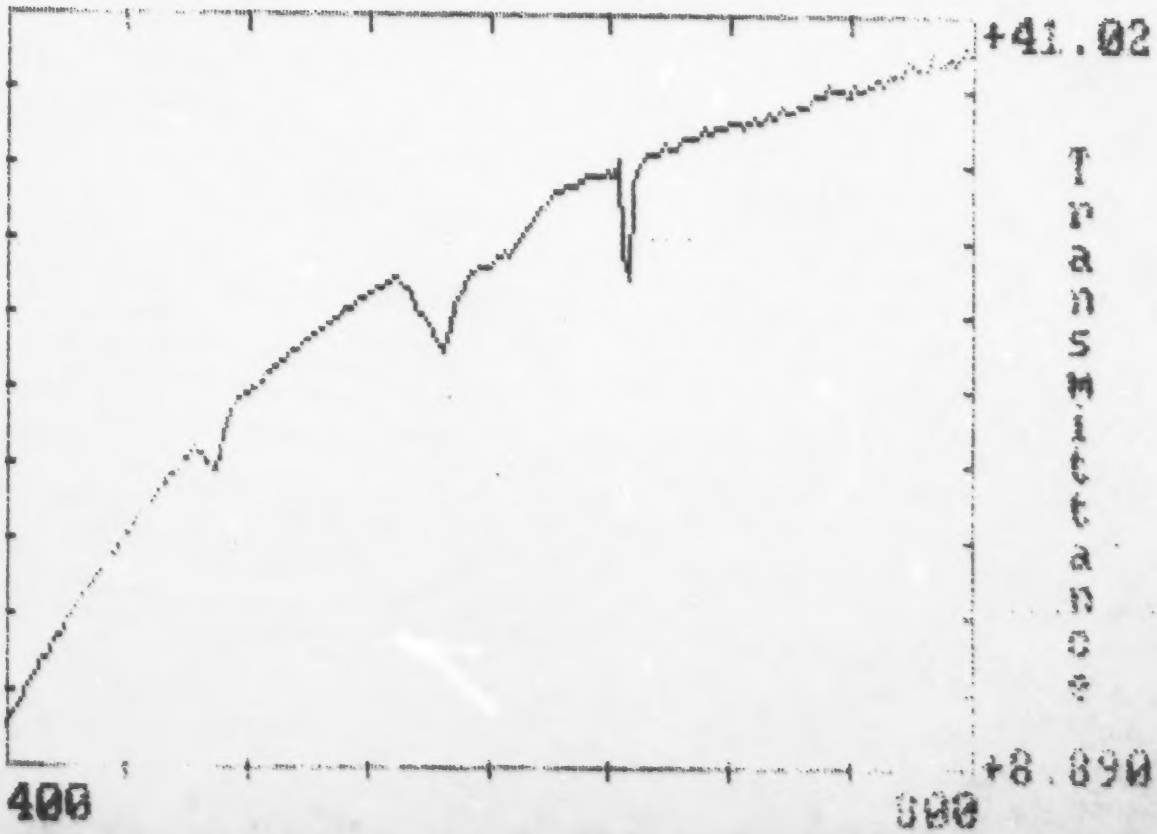

Fig 11

FIG.

---> WAVELENGTH SCAN REPORT <---

Aerogel
870723/K-E

Sample :
Solvent :
Concen :
Units :

Thickness 0.32 cm

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 second
Std Deviation : OFF

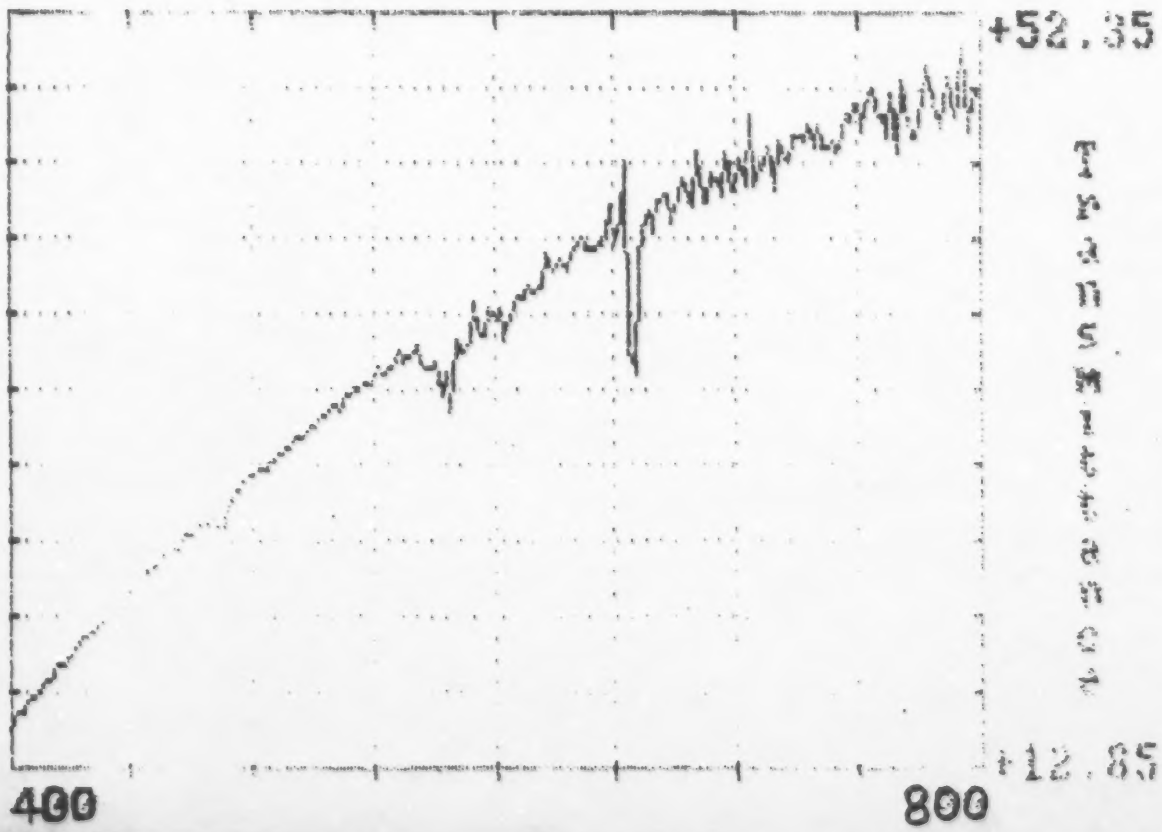

Fig. 12

FIG.

---> WAVELENGTH SCAN REPORT <---

Aerogel

Sample : 870722/K-B.

Solvent :

Concentration : Thickness 0.32cm

Units :

Date :

Time :

Operator :

Function : % transmittance

Wavelength Range : 400 to 800 nanometers

Integration Time : 1 second

Std Deviation : OFF

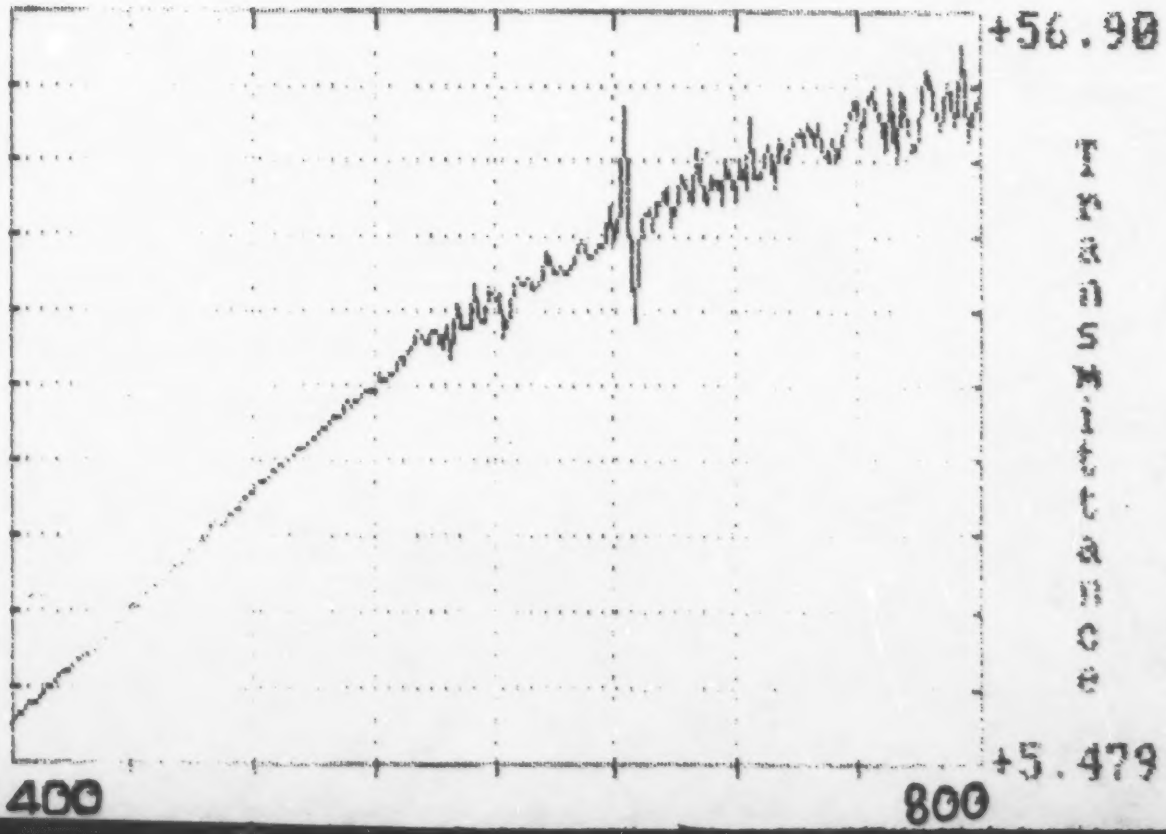

Fig 13.

FIG.

---> WAVELENGTH SCAN REPORT <---

Aerogel

Sample : 870723/k-c.1
Solvent :
Concentration : @ Thickness 0.33cm
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : Off

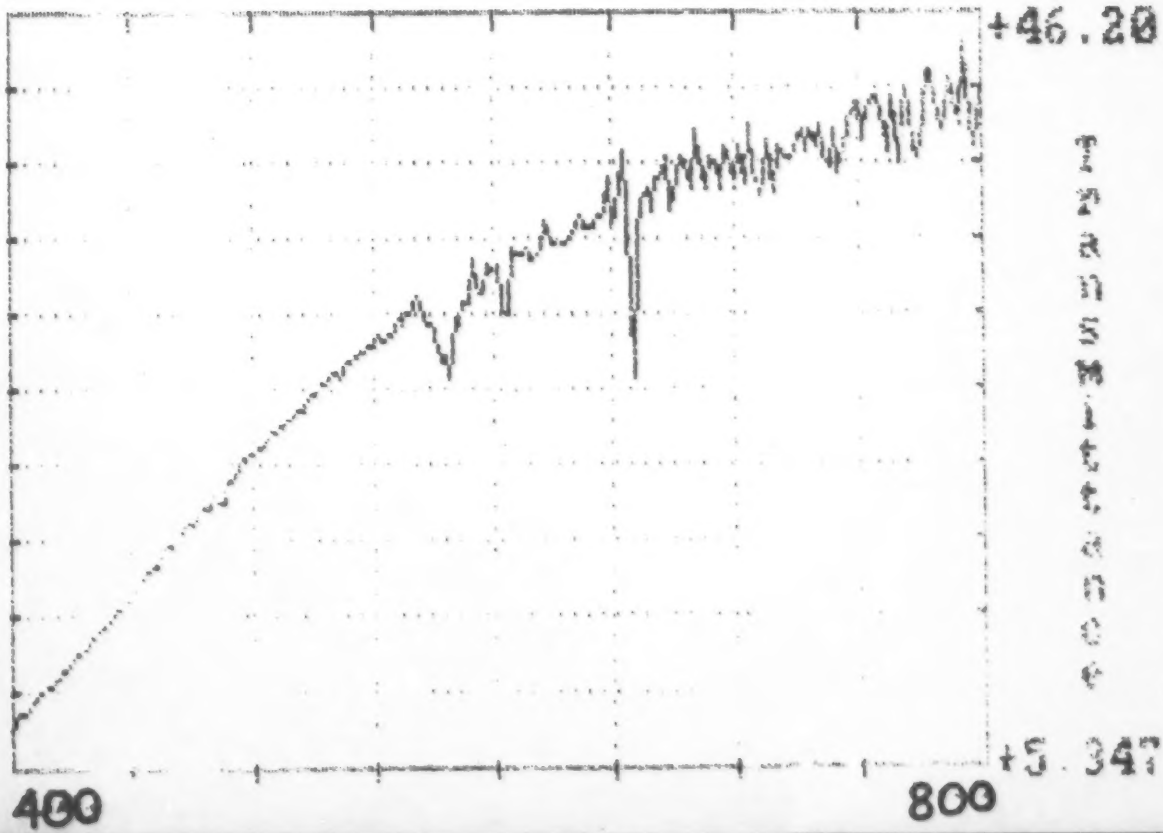

FIG 14

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---> WAVELENGTH SCAN REPORT <---

Sample Name : Aerogel pyrolysed at 500°C
870723/K-C-3
Concentration = Thickness 0.27 cm.
Units

Function : % Transmittance
Wavelength Range : 200 to 800 nanometers
Integration Time : 1 second
Std Deviation :

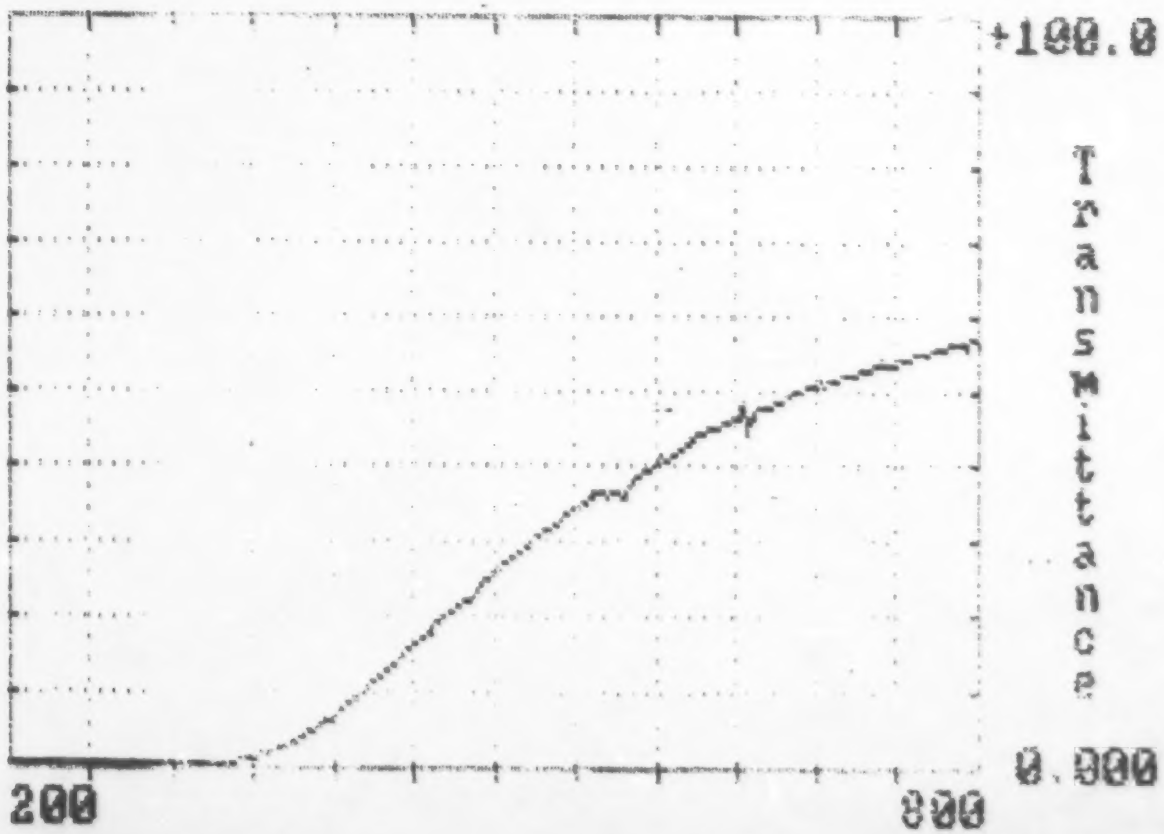

FIG. 15

27/1188

WAVELENGTH SCAN REPORT <---- 27 01 88

Aerogel 870806

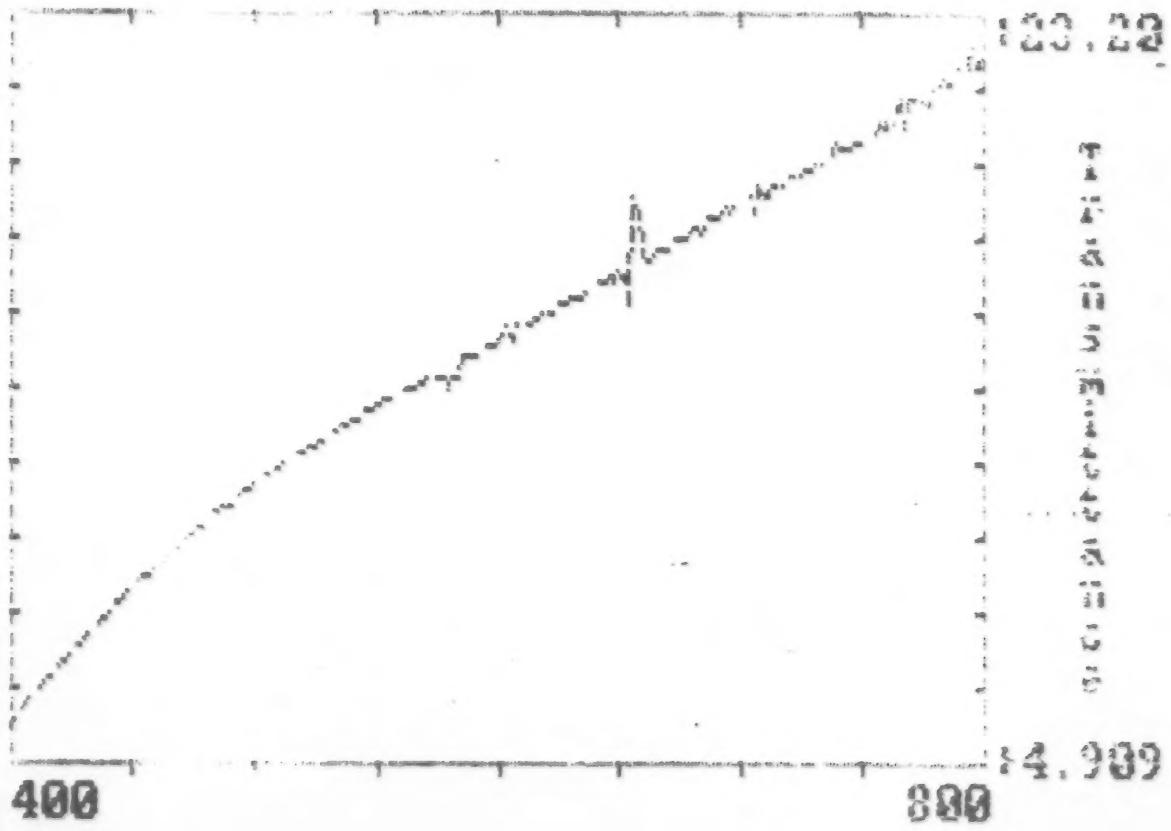

FIG. 16

---> WAVELENGTH SCAN REPORT <---

Date : [illegible]
Time : [illegible]
Operator : [illegible]

Sample No : 870626/K-A2(D)
Solvent No : [illegible]
Concentrat. : [illegible]
Units

Function : % Transmittance
Wavelength Range : 400 to [illegible] nanometers
Integration Time : 1 seconds
Std Deviation : OFF

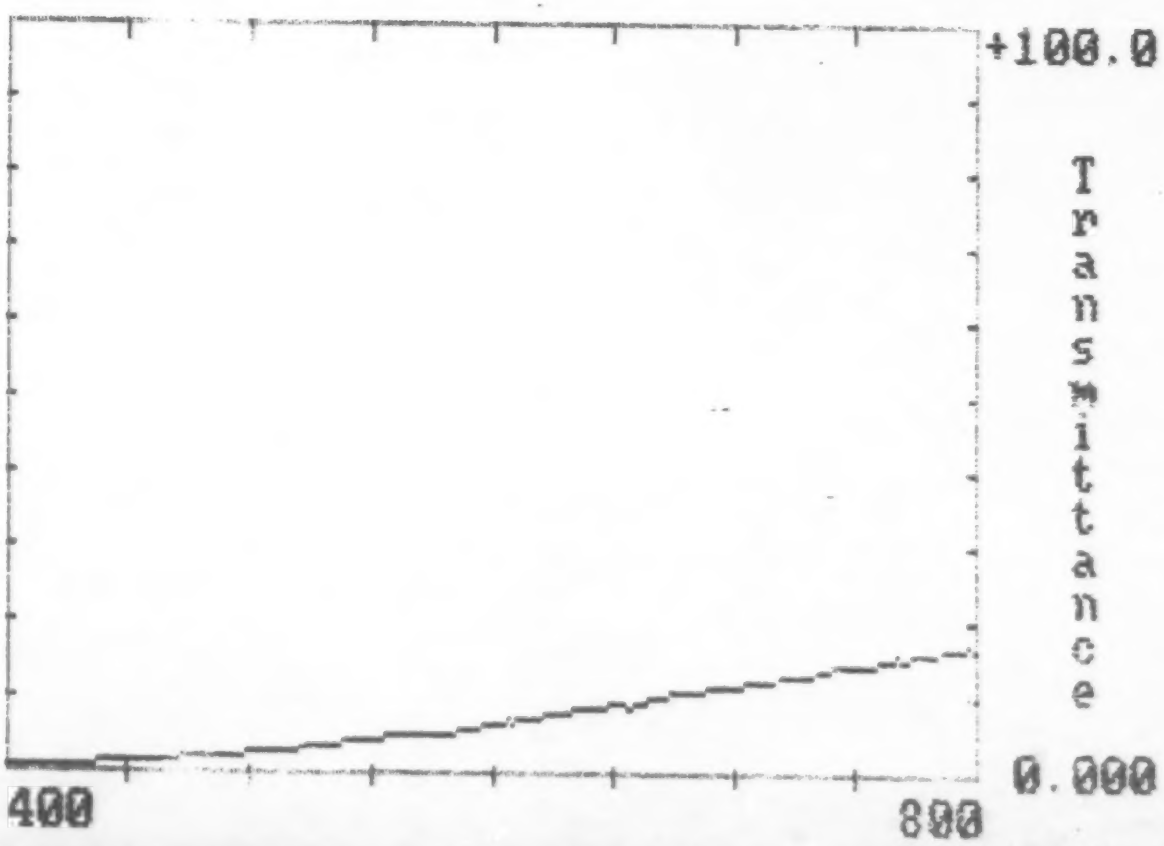

FIG 17

---> WAVELENGTH SCAN REPORT <---

Date : [illegible] 12/22/87
Time : [illegible]
Operator : [illegible]

Sample Name : 870814/2
Solvent Name :
Concentration : 0
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

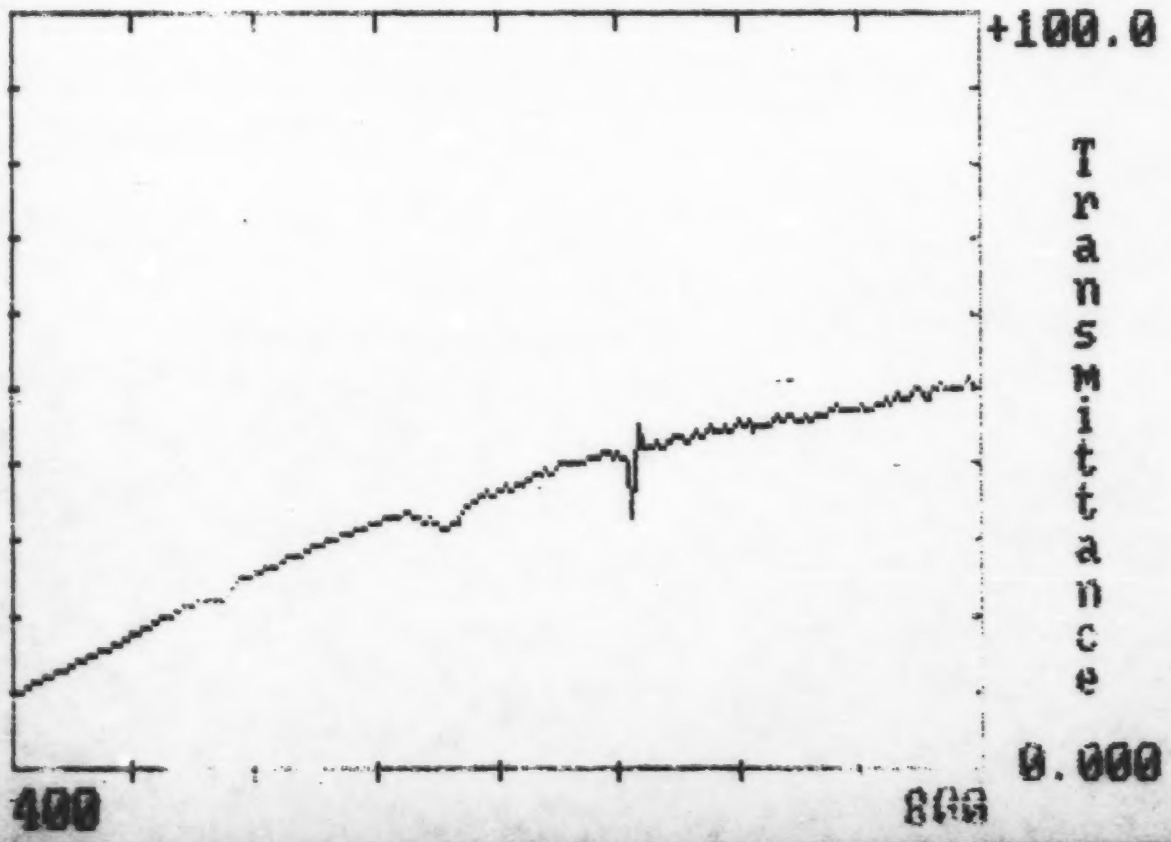

FIG. 18

---> WAVELENGTH SCAN REPORT <---

Date : 12/22/87
Time : [illegible]
Operator : [illegible]

Sample Name : 870703/K-A.2
Solvent Name :
Concentration :
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

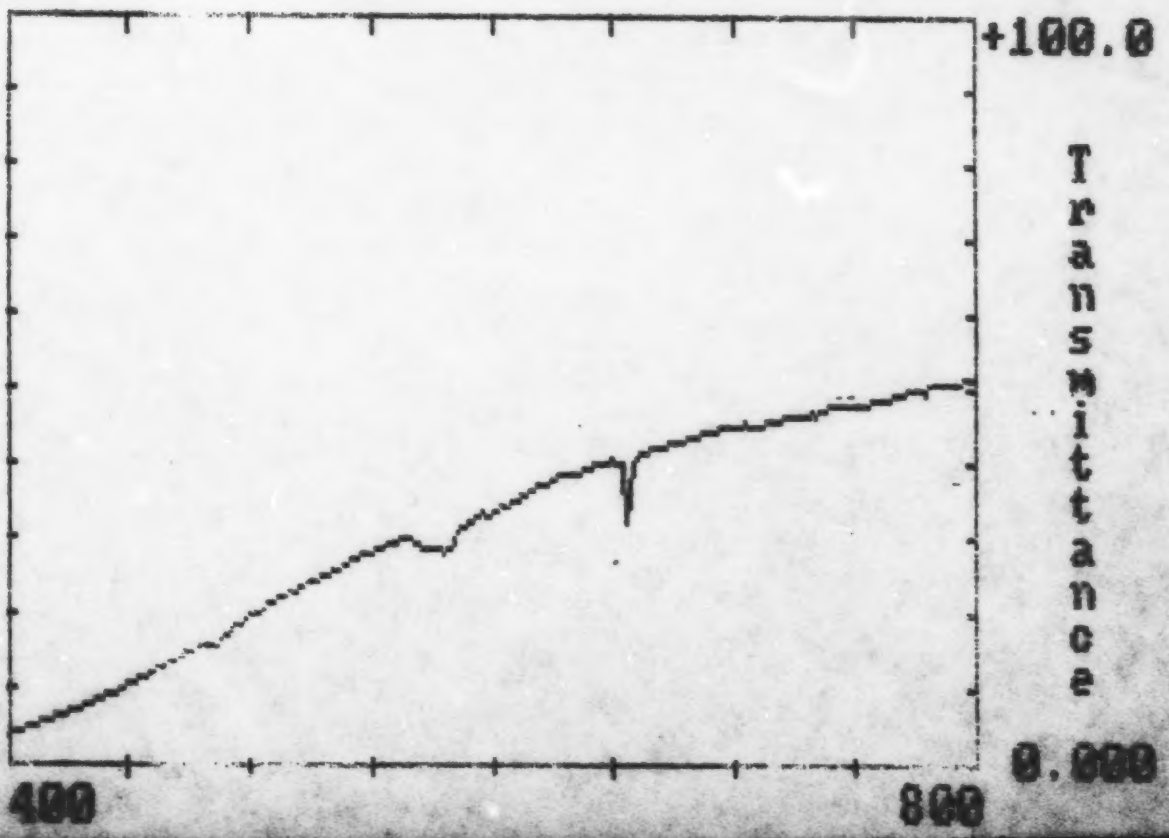

FIG 19

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---> WAVELENGTH SCAN REPORT <---

Date : [illegible]
Time : [illegible]
Operator : [illegible] PC6

Sample No: Aerogá 870723/k-0.1
Solvent No
Concentrat.
Units

Function : % Transmittance
Wavelength Range : [illegible]
Integration Time : [illegible]
Std Deviation : [illegible]

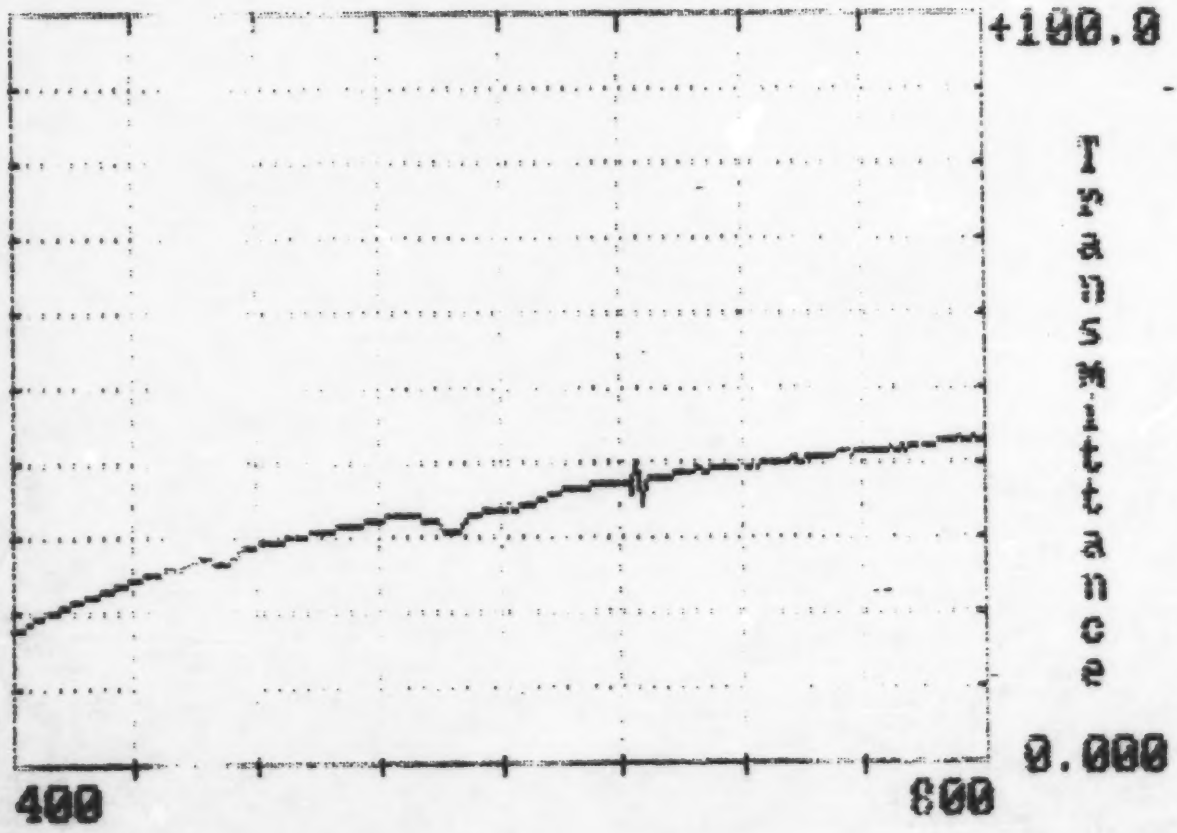

FIG 20

26/1/88

---> WAVELENGTH SCAN REPORT <---

Time
Operator PCG

Sample Avrgt 870814/1
Solvent
Concentration
Units

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 second
Std Deviation : OFF

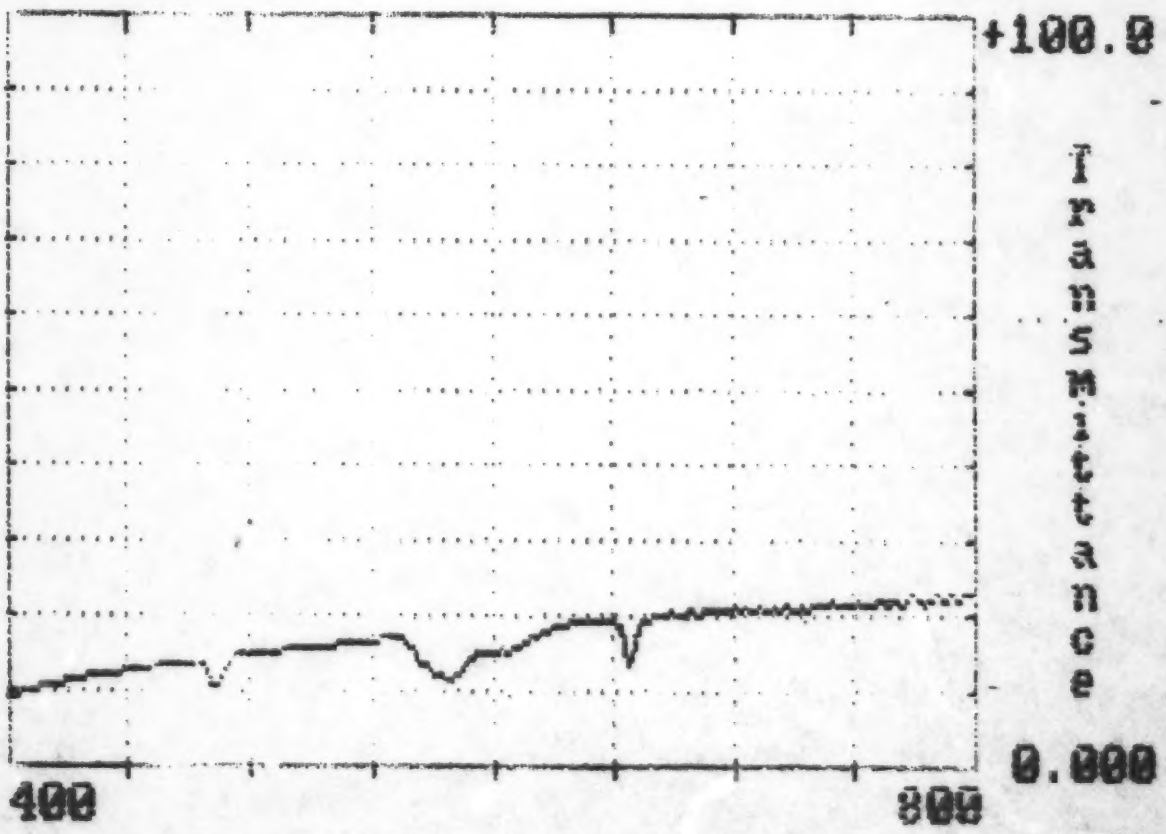

FIG. 21

26/1/88

---> WAVELENGTH SCAN REPORT <---

Date :
Time :
Operator : PCG

Sample No: Averged 870820
Solvent No:
Concentrat :
Units

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : UFS

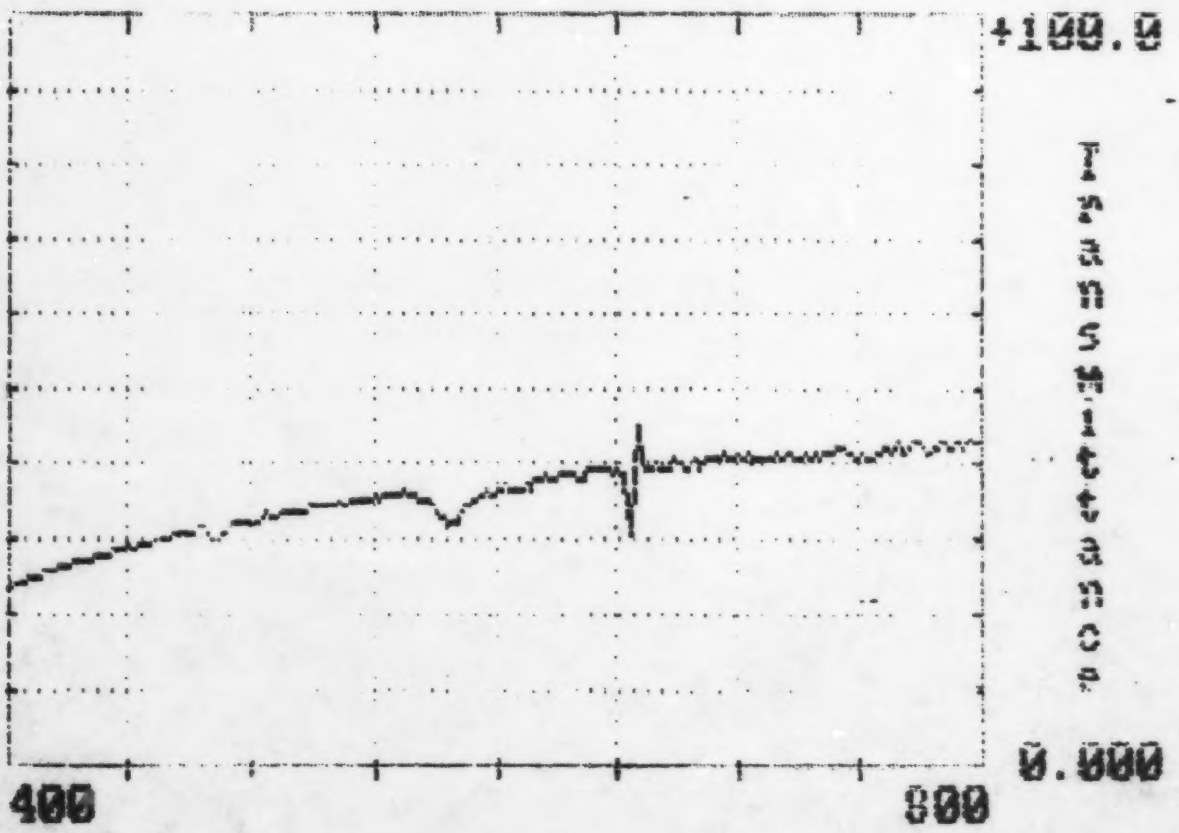

FIG. 22

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Sample Name : Aerogel
Solvent Name : 870812
Concentration : 4.7 mm thick
Units :

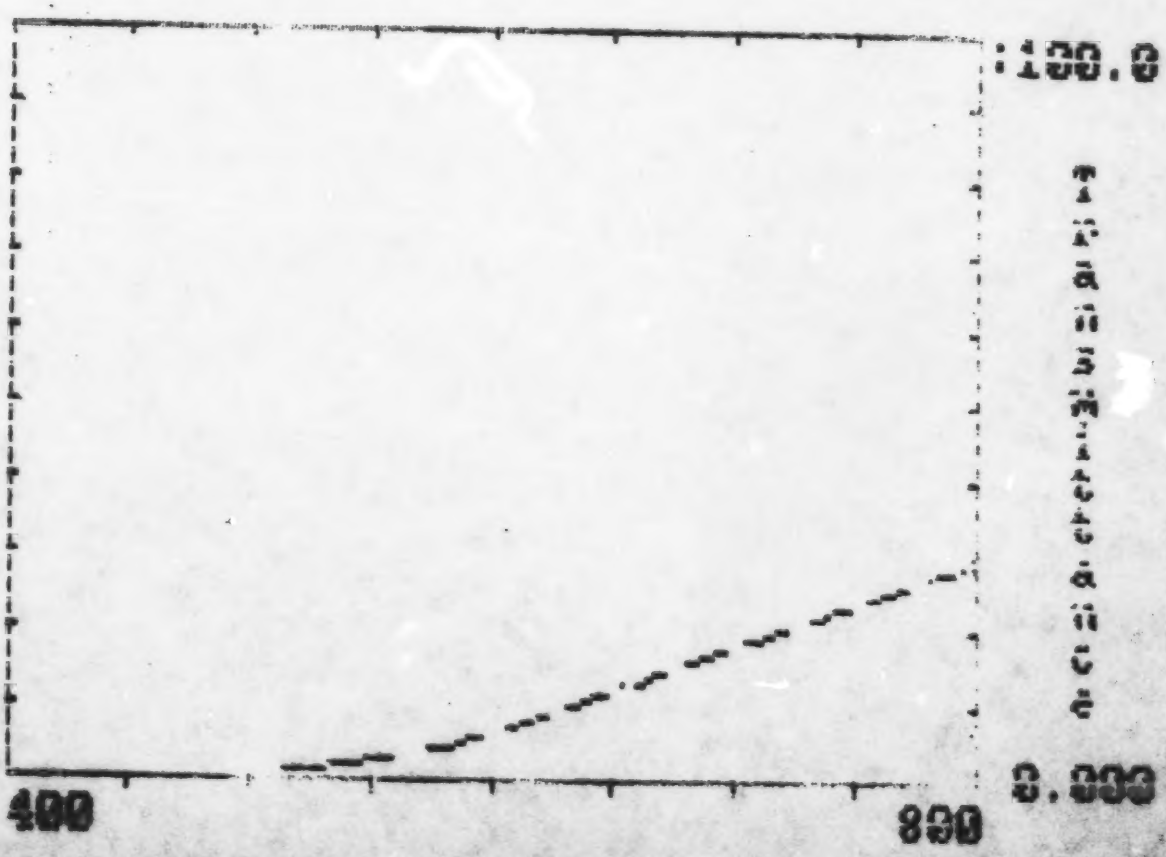


FIG. 23

25/2/88

Units : ~~[illegible]~~
Time : [illegible]
Operator : ~~[illegible]~~ P.C.G

---> WAVELENGTH SCAN REPORT <---

Sample Name : Aerogel
Solvent Name : 870630/k-A.2(D)
~~Concentration~~ : Thickness 0.35 cm
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

FIG. 24

---> WAVELENGTH SCAN REPORT <---

Date : 25/2/88
Time : 00:34:37
Operator : P.C.G

Sample Name : Aerogel
Solvent Name : 870703/K-A.3
~~Concentration~~ : Thickness 0.3 cm
Units :

Function : A Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

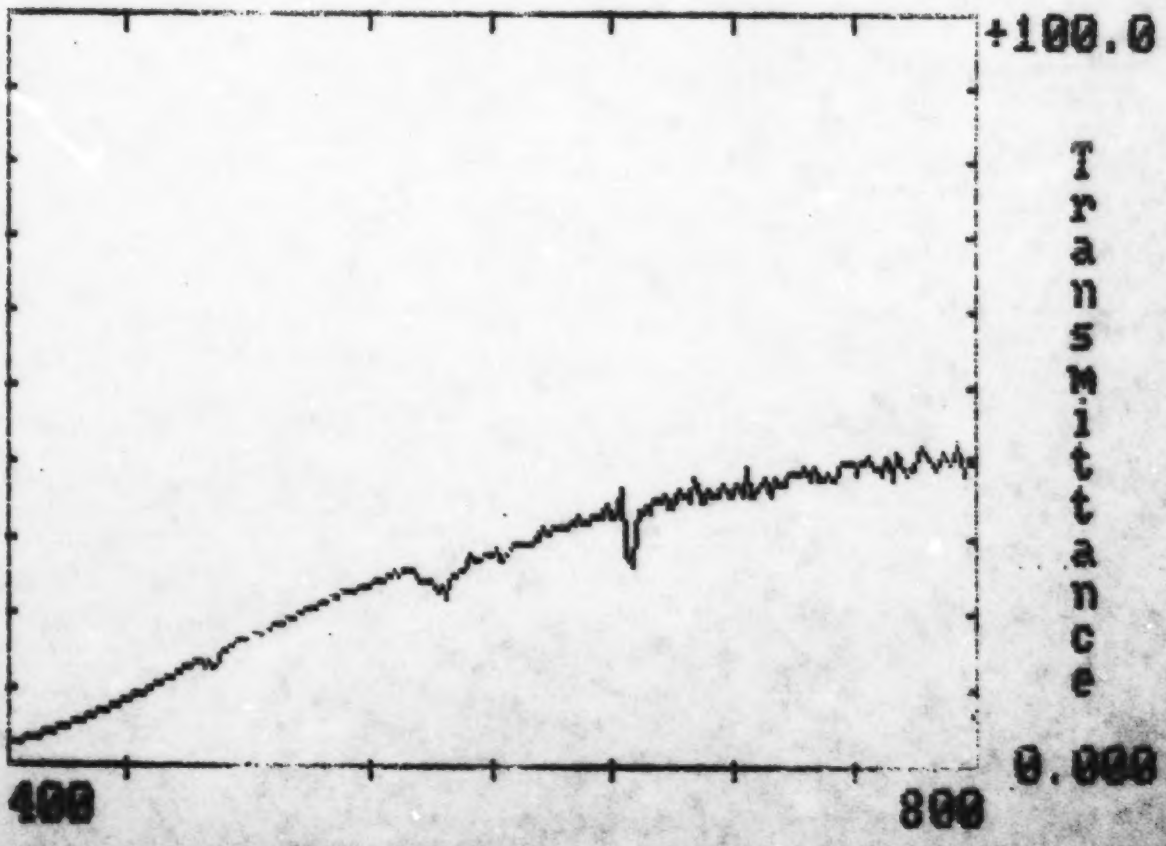


FIG. 25

25/2/88

---> WAVELENGTH SCAN REPORT <---

Time : [illegible]
Operator : [illegible] PCA

Sample Name : Aerogel
Solvent Name : 870821
Concentration : 0.46cm thick
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

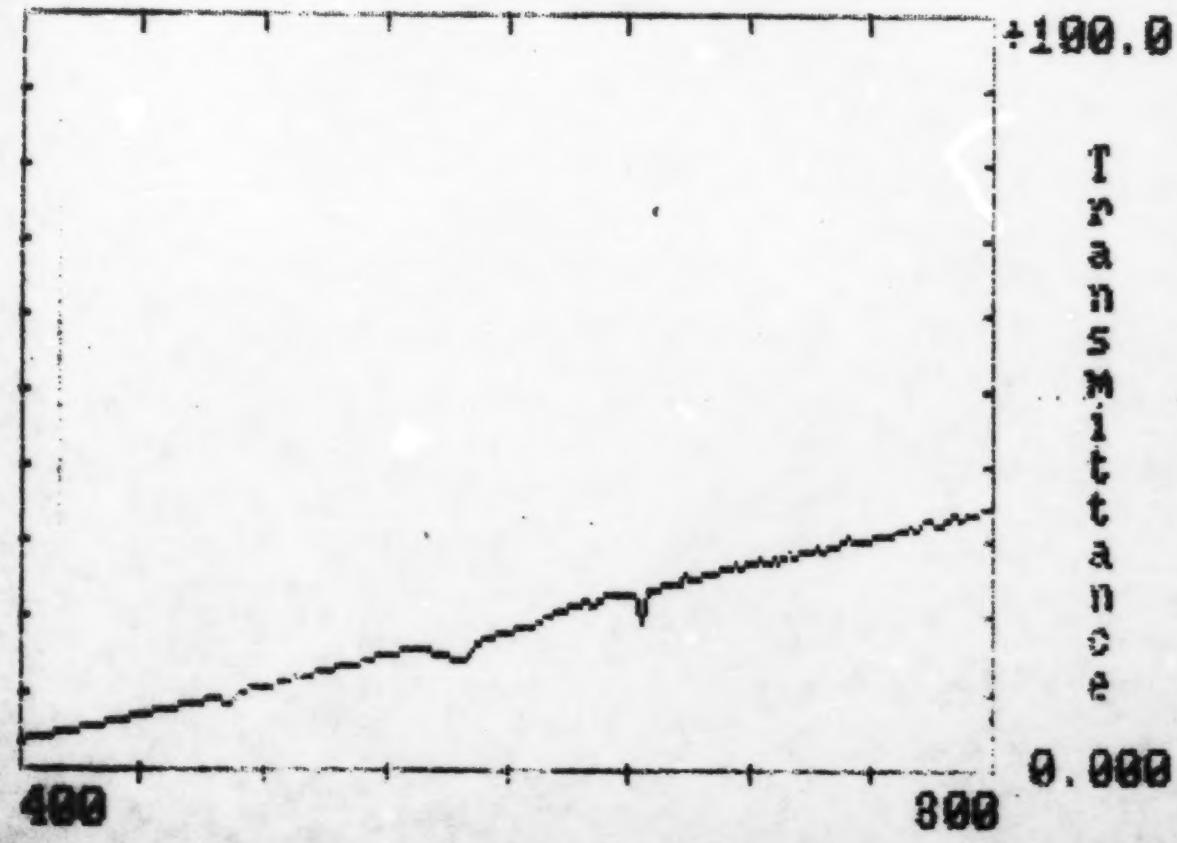


FIG. 26.

25|2|88

---> WAVELENGTH SCAN REPORT <---

Time : 00:45:0
Operator : P.C.G

Sample Name : Aerogel 870703/K-C.3
Solvent Name :
Concentration : Thickness 0.30cm
Units :

Function : % Transmittence
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

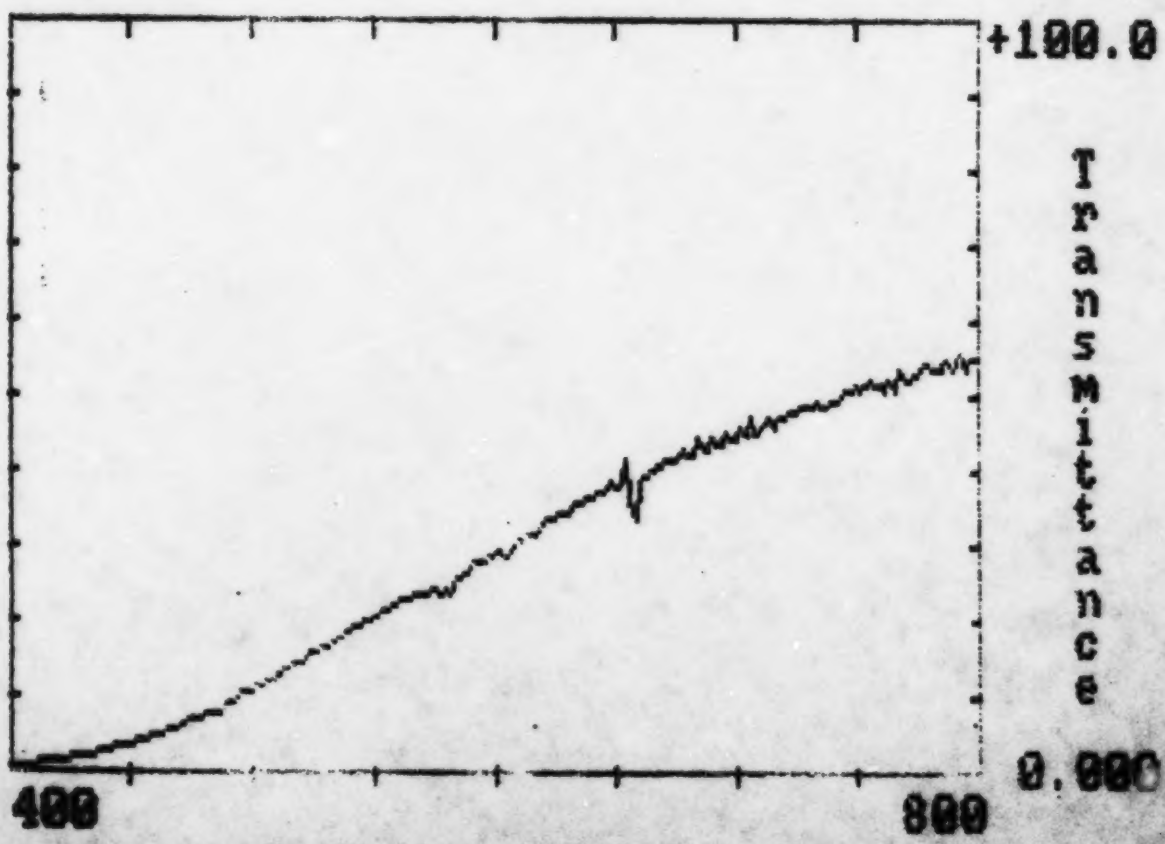


FIG. 27

25/2/88

---> WAVELENGTH SCAN REPORT <---

Date : ~~01-01-1980~~

Time : 00:40:40

Operator : ~~DIANNE SMART~~ P c.4

Sample Name : Aerogel 870707/K-B.3

Solvent Name : Thickness 0.40cm

~~Concentration~~ :

Units :

Function : % Transmittance

Wavelength Range : 400 to 800 nanometers

Integration Time : 1 seconds

Std Deviation : OFF

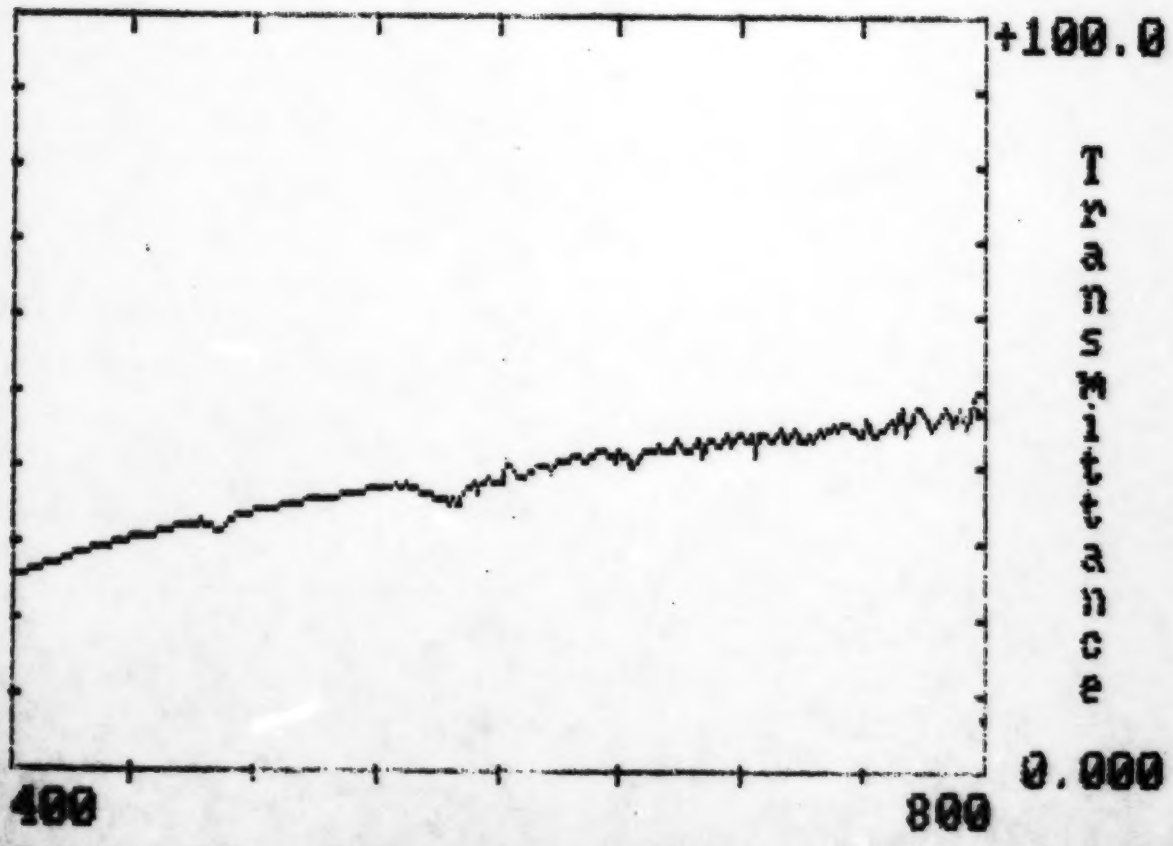


FIG. 23

---> WAVELENGTH SCAN REPORT <---

Time : [illegible]
Time : 00:46:28
Operator : DIANNE [illegible]

Sample Name : Aerogel 870626/K-A.2
~~Solvent Name~~ :
~~Concentration~~ : Thickness 0.30 cm
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

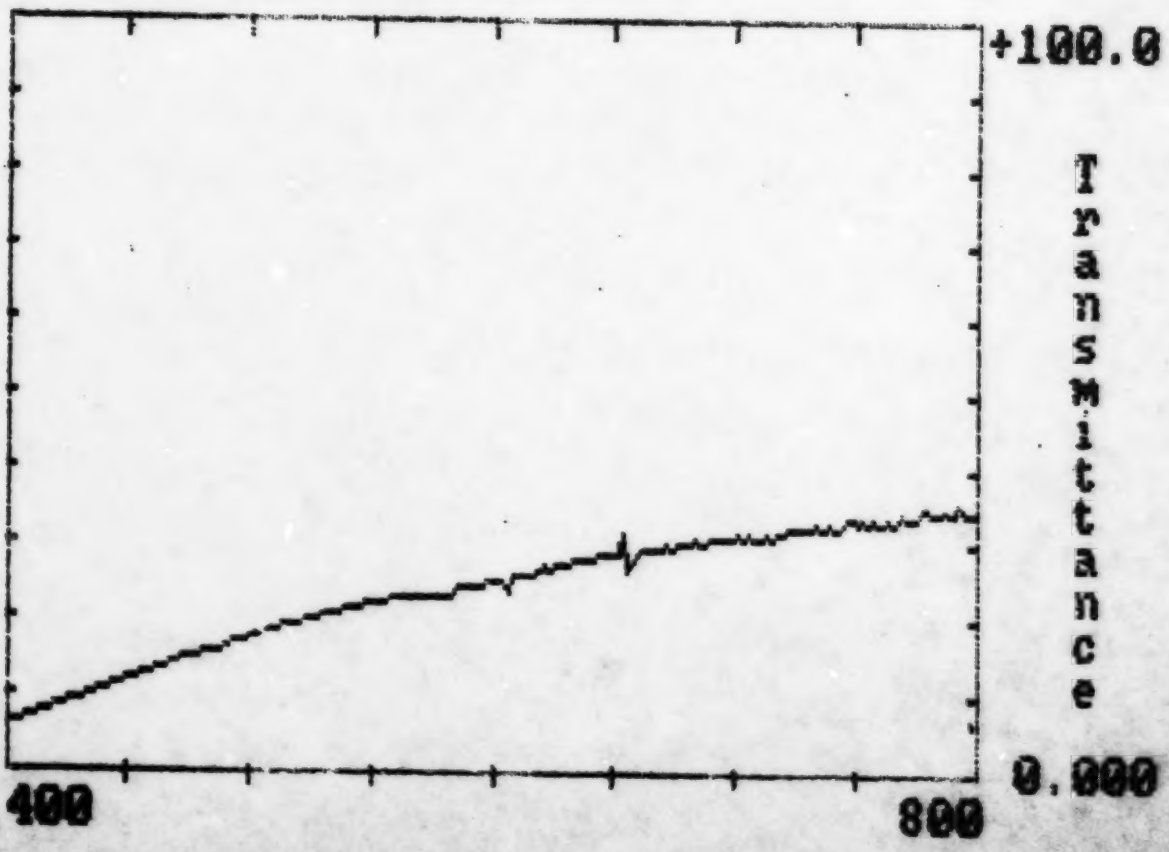


FIG. 29 :

25/2/88

---> WAVELENGTH SCAN REPORT <---

Time : [illegible]

Operator : ~~[illegible]~~ P.C.G

Aerogel

Sample Name : 880120

~~Solvent Name~~ Thickness: 0.17 cm

Concentration : 0

Units :

Function : % Transmittance

Wavelength Range : 400 to 800 nanometers

Integration Time : 1 seconds

Std Deviation : OFF

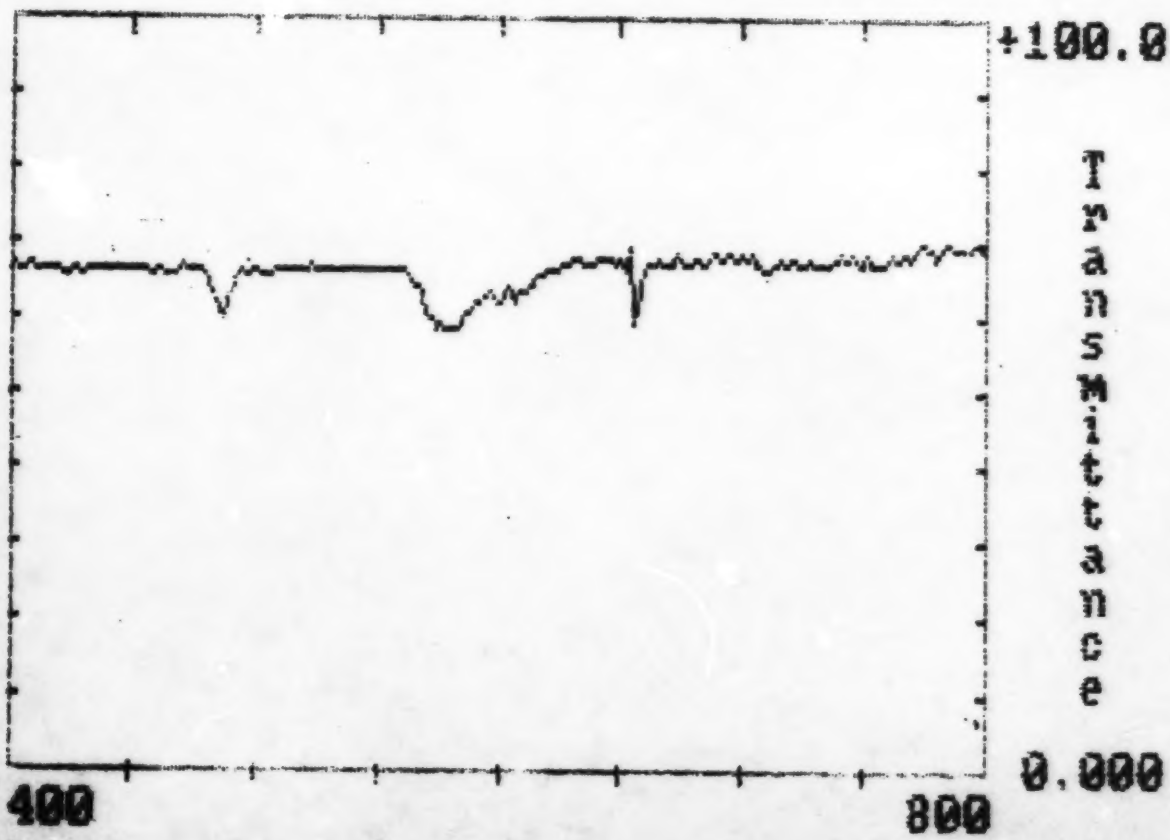


FIG. 30

25/2/88

---> WAVELENGTH SCAN REPORT <---

Time : 08.27.22

P C.G

Sample Name : Aerogel
Solvent Name : 870723/K-D3
~~Concentration~~ : Thickness 0.34 cm
Units :

Function : % Transmittance
Wavelength Range : 400 to 800 nanometers
Integration Time : 1 seconds
Std Deviation : OFF

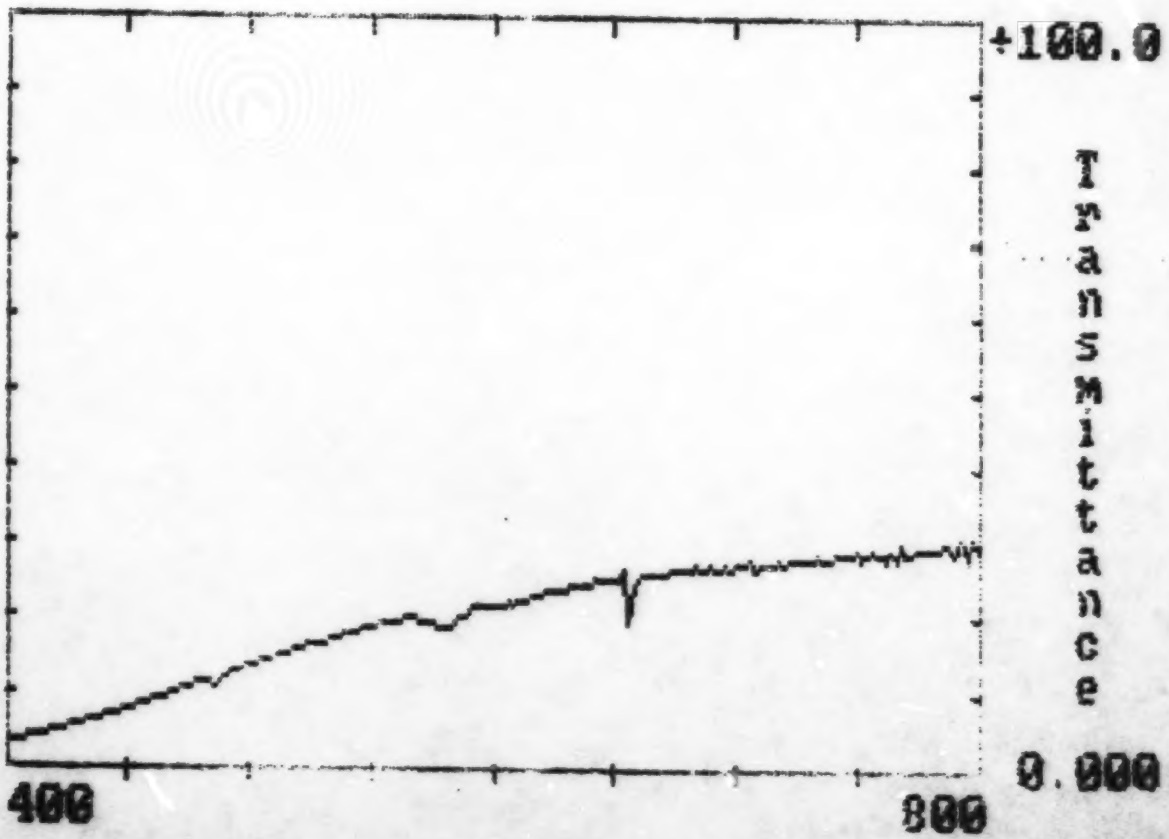


Fig. 31

28/3/88

WAVELENGTH SCAN REPORT

Aerogel
871214/2
2.5 mm Thick
pyrolyzed at 500C

PC4

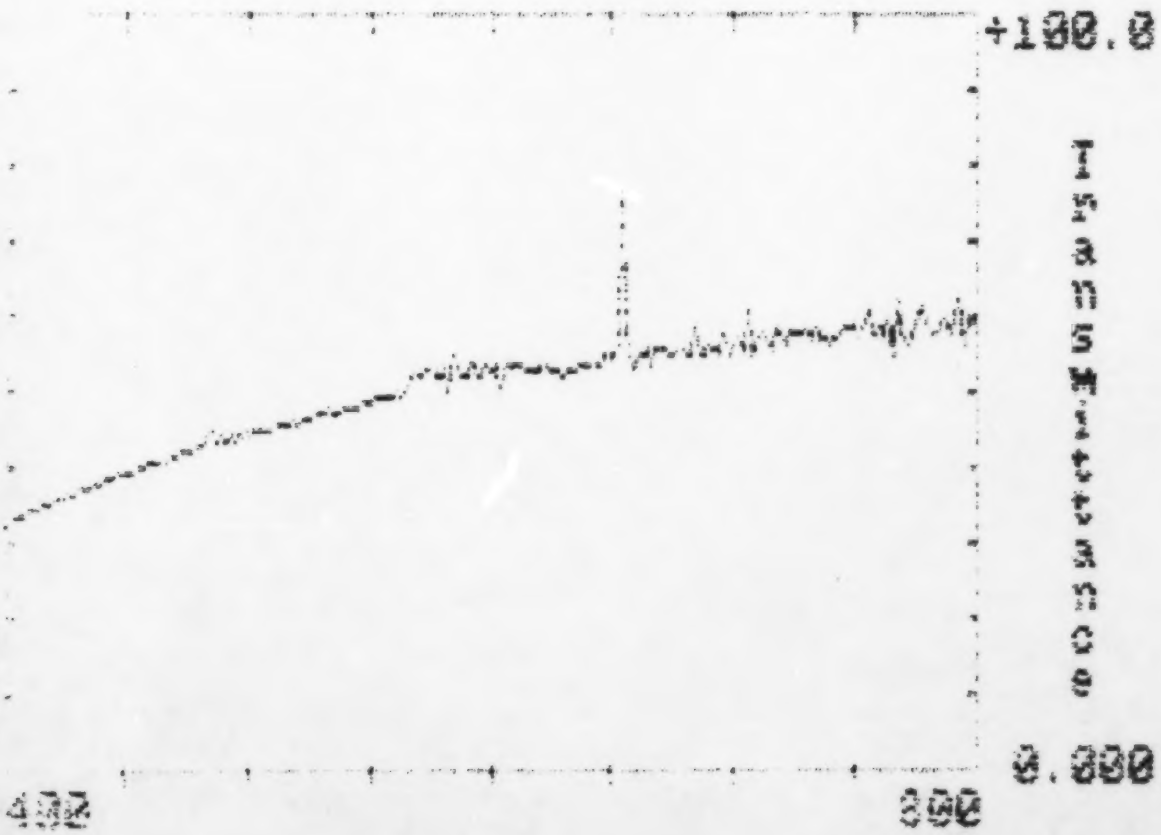
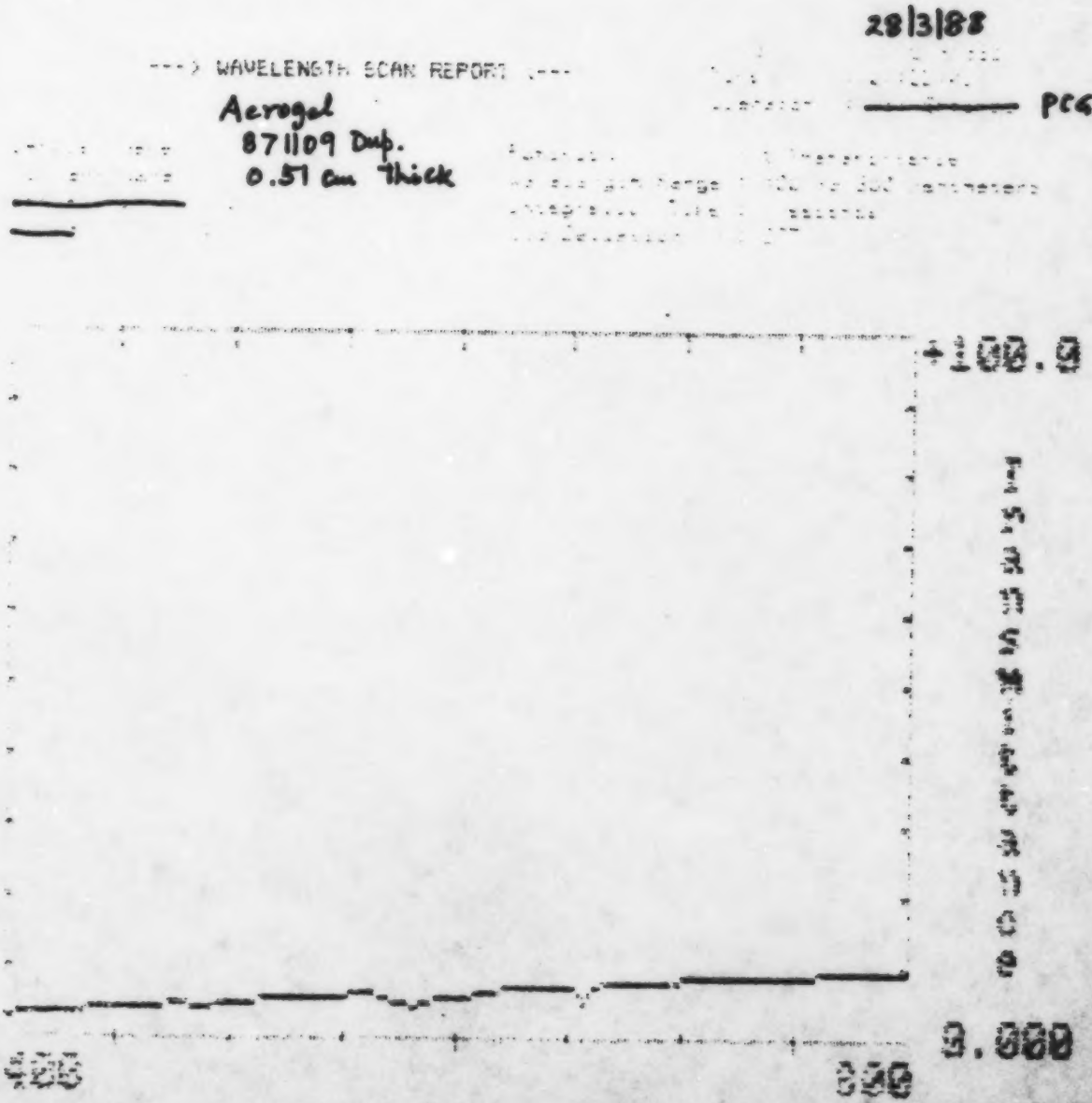
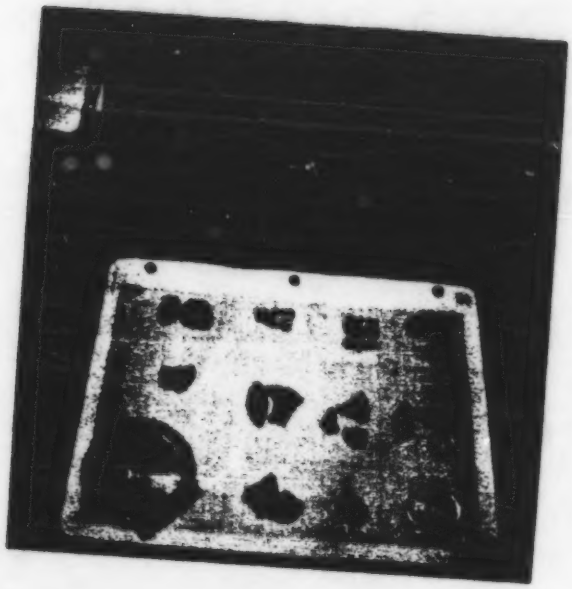
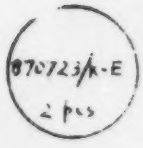


Fig. 32

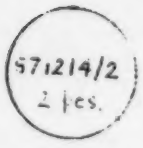

28|3|88
---> WAVELENGTH SCAN REPORT ---
Aerogel
87109 Dup.
0.51 cm Thick
PCC
+100.0
0.000
425
800

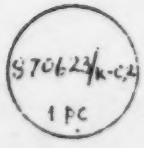


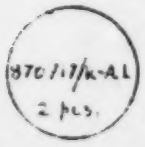

870723/A-E
2 pcs

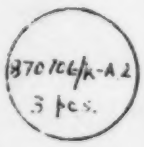
870806
1 pc.

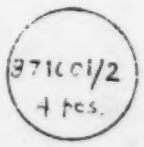
871109
2 pcs.


871214/2
2 pcs.


870623/A-C2
1 pc


870717/A-A1
2 pcs.


870706/A-A2
3 pcs.


871001/2
4 pcs.

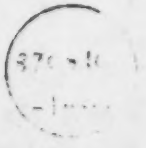
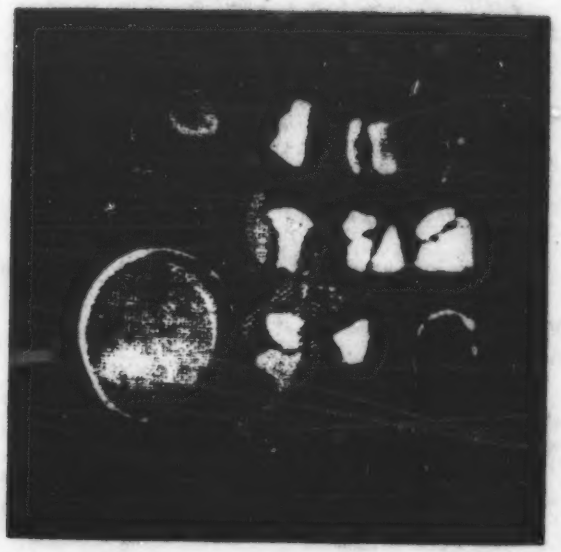


Figure [illegible]



870723/K-E
2 pcs

870806
1 pc.

871109
2 pcs.

871214/2
2 pcs.

870623/K-C2
1 pc.

870717/K-A1
2 pcs.

870706/K-A2
3 pcs.

871001/2
4 pcs.

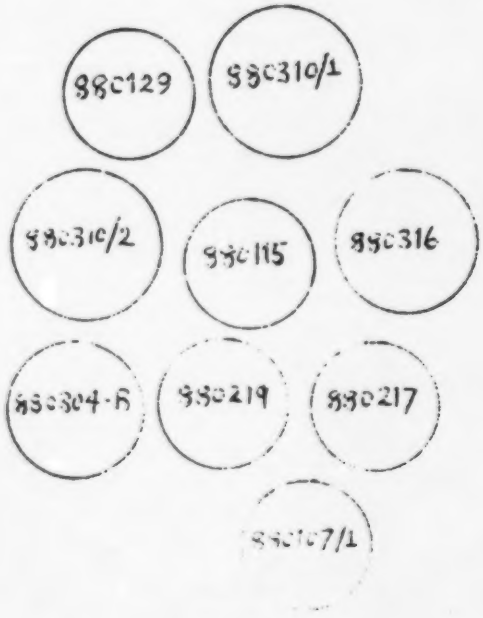
870724/K-B
(2 pcs)

870810
2 pieces

870723/K-E3
1 pc

[illegible]
[illegible]

Figure D


88c129
88c310/1
88c310/2
88c115
88c316
88c304-6
88c219
88c217
88c107/1